A PERTURBATION THEORY OF ISOELECTRONIC MOLECULES: APPLICATION TO CO BASED ON N_2 *

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ABSTRACT

A perturbation theory of heteronuclear diatomic molecules based on isoelectronic homonuclear diatomic molecules is developed. The heteronuclear molecule is regarded as the isoelectronic homonuclear molecule perturbed by a transfer of charge from one nucleus to the other. The molecular energy, equilibrium internuclear distance, dissociation energy, and electric dipole moment are considered. The Hartree-Fock approximations for calculating the effect of one-electron perturbations are also discussed.

The theory is applied to the isoelectronic molecules CO and N_2. By making use of the uncoupled Hartree-Fock approximation, the first-order wavefunction in the perturbation series is determined by the variational method. The calculated molecular energy of CO is too low and the dipole moment is too large in magnitude. However the calculated polarity is in agreement with the results of recent Hartree-Fock calculations at the equilibrium distance.

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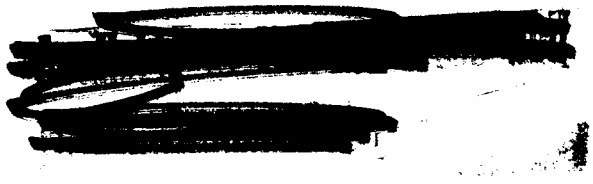

I. INTRODUCTION

The motivation for this investigation is the desire to compare the molecules CO and N_2, to understand their differences, and in particular the electric dipole moment of CO and its sign. The striking similarity of the two molecules can be seen from Table I: the bond distances differ by only 3 per cent, and although the dissociation energies differ by about 13 per cent, the total molecular energies are within 3.5 per cent of each other. The polarity of the dipole moment of CO is very difficult to determine, but was deduced indirectly to be $C^- O^+$ from microwave measurements of rotational magnetic moments and $J = 1 \leftarrow 0$ rotational frequencies for various isotopic species of CO. However, despite the initial support of this result by Ransil's Hartree-Fock calculation[2] using a minimum basis set, the recent Hartree-Fock calculations with enlarged basis sets[3,4] appears to be converging to a computed value of the dipole moment of CO equal in magnitude, but opposite in sign, to the accepted experimental value.[1,5] Nesbet[3] pointed out, in a critical discussion of the experimental determination[1] of the polarity of the CO dipole moment, that the sign of the polarity has not in fact been established definetely by experiment.

In this paper, a perturbation theory of heteronuclear diatomic molecules based on the isoelectronic homonuclear molecules is developed. The heteronuclear molecule is regarded as the isoelectronic homonuclear molecule perturbed by a transfer of charge from one nucleus to the other. The situation is favorable for such an approach since

the perturbation operator is simply a sum of one-electron terms. The molecular energy, equilibrium internuclear distance, dissociation energy, and electric dipole moment are considered in Section II. In Section III the various Hartree-Fock approximations for calculating the effect of one-electron perturbations are discussed. In Section IV the applicability of the perturbation theory is carefully considered and the theory is applied to the molecule CO based on N_2.

II. GENERAL THEORY FOR DIATOMIC MOLECULES

1. Molecular energy

Let the heteronuclear molecule AB of interest have nuclear charges

$$Z_A = Z_0(1+\lambda)$$

$$Z_B = Z_0(1-\lambda) \qquad (2.1)$$

and be taken to be the Z-perturbed condition of the isoelectronic homonuclear molecule CC with nuclear charges $Z_0 = (Z_A + Z_B)/2$. The electronic Hamiltonian of the Z-perturbed heteromolecule can be written

$$\mathcal{H} = \mathcal{H}_0 + \lambda V \qquad (2.2)$$

where $\mathcal{H}_0$ is the unperturbed electronic Hamiltonian and λ is the parameter

$$\lambda = (Z_A - Z_B)/(Z_A + Z_B). \qquad (2.3)$$

The perturbation V is a sum of one-electron operators

$$V = \sum_{i=1}^{N} Z_0 \left(r_{Bi}^{-1} - r_{Ai}^{-1} \right) \tag{2.4}$$

where r_{Ai} and r_{Bi} are the distances to the electron i from the nuclei A and B respectively. An important property of V is that it is antisymmetric with respect to inversion or interchange of nuclei A and B (u-symmetry).

The wavefunction Ψ for a particular nondegenerate electronic state and internuclear distance R of AB can be expanded in the familiar Rayleigh-Schrödinger power series in λ

$$\Psi = \Psi^{(0)} + \lambda \Psi^{(1)} + \mathcal{O}(\lambda^2) \tag{2.5}$$

Kato[6] has proved that the series converges for a perturbation such as Eq. (2.4), at least for small enough λ. $\Psi^{(0)}$ is the wavefunction of the homonuclear molecule for the same electronic state (i.e., that which is adiabatically correlated by changing λ) and internuclear distance R. We shall take Ψ and $\Psi^{(0)}$ to be normalized so that $\mathrm{Re} \langle \Psi^{(1)}, \Psi^{(0)} \rangle = 0$. The electronic energy expansion is

$$W = W^{(0)} + \lambda^2 W^{(2)} + \mathcal{O}(\lambda^4) \tag{2.6}$$

where the terms in odd powers of λ vanish by symmetry.* $W^{(0)}$ is the

*This can be seen by observing that the energy must be invariant to an interchange of nuclei A and B, i.e., $\lambda \rightarrow -\lambda$.

electronic energy of the unperturbed homonuclear molecule, and the second-order energy coefficient $W^{(2)}$ is given by

$$W^{(2)} = \langle \Psi^{(0)}, V \Psi^{(1)} \rangle . \tag{2.7}$$

The molecular energy E of a diatomic molecule is the sum of the electronic energy W and the nuclear repulsion energy;

$$E(R) = W(R) + Z_A Z_B / R . \tag{2.8}$$

Hence by using Eqs. (2.1) and (2.6), we obtain

$$E - E^{(0)} = \lambda^2 \left(W^{(2)} - Z_0^2 / R \right) + O(\lambda^4) . \tag{2.9}$$

Since $W^{(2)}$ must be negative for a ground state, it follows that the molecular energy E of the heteronuclear molecule must be lower than that of the homonuclear molecule $E^{(0)}$ at least for small λ .

2. Equilibrium internuclear distance

Let R_0 be the equilibrium internuclear distance for the homonuclear molecule CC ; that is

$$\left(\frac{dE^{(0)}}{dR} \right)_0 \equiv \left(\frac{dE^{(0)}}{dR} \right)_{R=R_0} = 0 . \tag{2.10}$$

Similarly let R_e be the equilibrium internuclear distance for the heteronuclear molecule AB; that is

$$\left(\frac{dE}{dR}\right)_e \equiv \left(\frac{dE}{dR}\right)_{R=R_e} = 0 . \tag{2.11}$$

Differentiating Eq. (2.9) with respect to R we have

$$\frac{dE}{dR} - \frac{dE^{(0)}}{dR} = \lambda^2\left(\frac{dW^{(2)}}{dR} + \frac{Z_0^2}{R^2}\right) + O(\lambda^4) . \tag{2.12}$$

If we put $R=R_e$ and expand $dE^{(0)}/dR$ about R_0, we obtain

$$-(R_e-R_0)\left(\frac{d^2E^{(0)}}{dR^2}\right)_0 + \cdots = \lambda^2\left[\left(\frac{dW^{(2)}}{dR}\right)_e + \frac{Z_0^2}{R_e^2}\right] + \cdots , \tag{2.13a}$$

or

$$R_e - R_0 = -\frac{\lambda^2}{k_0}\left[\left(\frac{dW^{(2)}}{dR}\right)_e + \frac{Z_0^2}{R_e^2}\right] + O(\lambda^4) \tag{2.13b}$$

where $k_0 = (d^2E^{(0)}/dR^2)_0$ is the force-constant of the homonuclear molecule. Thus $R_e - R_0$ is of order λ^2, and the sign depends on the relative magnitude of the two terms in the square brackets; $dW^{(2)}/dR$ will be negative in general because $W^{(2)}$ is negative at $R=\infty$ and becomes zero at $R=0$.

3. Dissociation energy

The dissociation energy of the heteronuclear molecule AB, D_e, and that of the homonuclear molecule, D_0, are given by

$$D_e = E(\infty) - E(R_e)$$
$$D_0 = E^{(0)}(\infty) - E^{(0)}(R_0) \quad . \tag{2.14}$$

Expanding $E(R_e)$ about R_0, we have

$$E(R_e) = E(R_0) + (R_e - R_0)\left(\frac{dE}{dR}\right)_0 + \cdots \quad . \tag{2.15}$$

Using Eqs. (2.12) and (2.13), we get

$$E(R_e) = E(R_0) + \mathcal{O}(\lambda^4) \quad . \tag{2.16}$$

Hence making use of Eqs. (2.9) and (2.16), we obtain

$$D_0 - D_e = \lambda^2 \left[\Delta W^{(2)}(R_0) - Z_0^2/R_0\right] + \mathcal{O}(\lambda^4) \tag{2.17}$$

where

$$\Delta W^{(2)}(R_0) = W^{(2)}(R_0) - W^{(2)}(\infty) \quad . \tag{2.18}$$

Since $\Delta W^{(2)}(R_0) > 0$ in general, the sign of $D_0 - D_e$ depends on the relative magnitude of the two terms in Eq. (2.17).

4. Electric dipole moment

The dipole moment of the heteronuclear molecule AB is

$$\langle \mu \rangle = \langle \Psi, \mu \Psi \rangle$$
$$= \langle \Psi^{(0)}, \mu \Psi^{(0)} \rangle + 2\lambda \langle \Psi^{(1)}, \mu \Psi^{(0)} \rangle + O(\lambda^3) \tag{2.19}$$

where A is taken to be on the Z-axis at $R/2$ and B to be at $-R/2$, Ψ is assumed to be real for simplicity and

$$\mu = -\sum_{i=1}^{N} z_i + \lambda Z_0 R \tag{2.20}$$

The dipole moment expression can only contain odd powers of λ since it changes sign if λ changes sign. Hence, using Eq. (2.20), we get

$$\langle \mu \rangle = \lambda \left(Z_0 R + 2 \langle \Psi^{(1)}, \mu \Psi^{(0)} \rangle \right) + O(\lambda^3) \; ; \tag{2.21}$$

the dipole moment has been defined to be negative for $A^- B^+$.

The terms in Eq. (2.21) tend to cancel since $\langle \Psi^{(1)}, \mu \Psi^{(0)} \rangle$ is almost certainly negative. To see this consider the spectral expansion in terms of the unperturbed eigenfunctions $\Psi_n^{(0)}$:

$$\langle \Psi^{(1)}, \mu \Psi^{(0)} \rangle = \sum_{n \neq 0} \frac{V_{on} \mu_{no}}{E_0 - E_n} \; . \tag{2.22}$$

The operator v_i and μ_i for one electron are sketched in Fig. 1. The important point to notice is that both V and μ have u-symmetry, so that $v\mu \geq 0$ everywhere. This means that $V_{on}\mu_{no} \geq 0$ for the lower excited states, and could only be negative if the transititon density

ρ_{no} has different signs where V is the largest and where μ is the largest. This is only likely to occur for highly excited states, if at all. Since $E_0 - E_n < 0$, we conclude that $\langle \Psi^{(1)}, \mu \Psi^{(0)} \rangle$, the dipole due to the electronic charge shift caused by the Σ -perturbation, is negative. This conclusion is supported by the Unsöld approximation for the sum in Eq. (2.22), which replaces the increasing denominators $E_0 - E_n$ by that of the smallest non-vanishing term, say $E_0 - E_1$:

$$\langle \Psi^{(1)}, \mu \Psi^{(0)} \rangle \simeq \frac{\langle \Psi^{(0)}, V\mu \Psi^{(0)} \rangle}{E_0 - E_1} \quad . \tag{2.23}$$

This approximate expression is necessarily negative.

To decide the sign of $\langle \mu \rangle$ it is therefore necessary to perform an accurate calculation of the electronic term. It is interesting to note that by Dalgarno's interchange theorem [7,8] this can be written in the alternative form

$$\langle \Psi^{(1)}, \mu \Psi^{(0)} \rangle = \langle \chi^{(1)}, V \Psi^{(0)} \rangle \tag{2.24}$$

where $\chi^{(1)}$ is the solution of the equation

$$(\mathcal{H}_0 - E^{(0)}) \chi^{(1)} + (\mu - \lambda z_0 R) \Psi^{(0)} = 0 \quad . \tag{2.25}$$

Since both V and μ are one-electron operators the interchanged form does not possess any obvious advantage.

5. Schwartz discriminant

A simple check on the validity of merely taking the leading terms in the power series for $W-W^{(0)}$ in Eq. (2.6) and for $\langle \mu \rangle$ in Eq. (2.21) is provided by the Schwartz-like inequality

$$\sum_{n\neq 0} \frac{V_{no}^2}{E_0-E_n} \sum_{n\neq 0} \frac{\mu_{no}^2}{E_0-E_n} \geq \left(\sum_{n\neq 0} \frac{V_{on}\mu_{no}}{E_0-E_n} \right)^2 . \tag{2.26}$$

Using Eqs. (2.6), (2.21) and (2.22), we obtain

$$\left(\frac{W^{(0)}-W}{\lambda^2} \right) \left(\frac{\alpha}{2} \right) \geq \left(\frac{\lambda Z_0 R - \langle \mu \rangle}{2\lambda} \right)^2 \tag{2.27a}$$

or

$$W^{(0)} - W \geq \frac{(\lambda Z_0 R - \langle \mu \rangle)^2}{2\alpha} \tag{2.27b}$$

where α is the polarizability of the homonuclear molecule parallel to the axis, given by

$$\alpha = -2 \sum_{n\neq 0} \frac{\mu_{on}^2}{E_0 - E_n} . \tag{2.28}$$

This inequality is checked below for the case of CO and N_2.

6. Energy difference for separated atoms

The electronic energy differnece at the infinite internuclear separation, $[W(\infty) - W^{(0)}(\infty)]$, can be easily computed using the $1/Z$ -expansion for the atomic energies. For an atom with nuclear charge Z_0 and N electrons, the electronic energy can be expanded as follows

$$\mathcal{E}(Z_0, N) = Z_0^2 \epsilon^{(0)}(N) + Z_0 \epsilon^{(1)}(N) + \epsilon^{(2)}(N) + \epsilon^{(3)}(N)/Z_0 + \mathcal{O}(1/Z_0^2) . \tag{2.29}$$

For the perturbed condition, that is, an atom with nuclear charge $Z_0(1+\lambda)$ and an atom with nuclear charge $Z_0(1-\lambda)$, the total energy is

$$\begin{aligned} W(\infty) &= \mathcal{E}[Z_0(1+\lambda), N] + \mathcal{E}[Z_0(1-\lambda), N] \\ &= 2\{ Z_0^2 \epsilon^{(0)}(N) + Z_0 \epsilon^{(1)}(N) + \epsilon^{(2)}(N) + \epsilon^{(3)}(N)/Z_0 + \cdots \} \\ &\quad + 2\lambda^2 \{ Z_0^2 \epsilon^{(0)}(N) + \epsilon^{(3)}(N)/Z_0 + \cdots \} \\ &\quad + 2\lambda^4 \{ \epsilon^{(3)}(N)/Z_0 + \cdots \} . \end{aligned} \tag{2.30}$$

Since $W^{(0)}(\infty) = 2\mathcal{E}(Z_0, N)$, the energy difference is given by

$$W(\infty) - W^{(0)}(\infty) = 2\lambda^2 \{ Z_0^2 \epsilon^{(0)}(N) + \epsilon^{(3)}(N)/Z_0 + \cdots \} + \mathcal{O}(\lambda^4) . \tag{2.31}$$

That is, by Eq. (7)

$$W^{(2)}(\infty) = 2\{ Z_0^2 \epsilon^{(0)}(N) + \epsilon^{(3)}(N)/Z_0 + \mathcal{O}(1/Z_0^2) \} . \tag{2.32}$$

The interesting feature is that $W^{(2)}(\infty)$ contains neither the average repulsion term $\epsilon^{(1)}(N)$ nor the second order term $\epsilon^{(2)}(N)$. The third order term $\epsilon^{(3)}(N)$ is expected to be very much smaller than $\epsilon^{(0)}(N)$. If the ith electron in a hydrogenic orbital has principal quantum number n_i, then

$$\epsilon^{(0)}(N) = -\frac{1}{2}\sum_{i=1}^{N}\frac{1}{n_i^2} \quad . \tag{2.33}$$

Note that if $Z_A = Z_0 + 1$ and $Z_B = Z_0 - 1$, so that $\lambda Z_0 = 1$, then

$$\mathcal{E}(Z_A,N)+\mathcal{E}(Z_B,N)-2\mathcal{E}(Z_0,N) \simeq -\sum_{i=1}^{N}\frac{1}{n_i^2} \quad . \tag{2.34}$$

This corresponds to the energy difference between the ion pair $A^+ + B^-$ and two neutral atoms, C, each having N electrons.

III. THE HARTREE-FOCK APPROXIMATION

In this section the calculation of the effect of a one-electron perturbation on an atomic or molecular system is discussed. It has already been pointed out that the perturbation V [Eq. (2.4)] is a sum of one-electron terms. Any practical calculation of the perturbation effect will have errors due to the actual solving of the perturbation equation and to the inevitable inaccuracy of the unperturbed wavefunction. The latter source of error may be more serious, and hence the Hartree-Fock approximation is of special

importance in treating the unperturbed and perturbed systems on an equal basis.

Since a comprehensive review paper on the calculation of the effect of one-electron perturbations on atoms has recently appeared[9] the Hartree-Fock approximation alone will be discussed.

1. The coupled Hartree-Fock approximation[10-12]

To avoid mathematical complexity we suppose the atomic or molecular system has a closed shell configuration. Then in the Hartree-Fock approximation to the perturbed system the perturbed wavefunction is written as

$$\Psi = \mathcal{A} \prod_{i=1}^{2n} \varphi_i(i) \tag{3.1}$$

where $\mathcal{A}$ is the normalized antisymmetrizing operater. Restricting the problem to a scalar, one-electron perturbing potential in first-order,

$$V = \lambda \sum_i v(i) \tag{3.2}$$

the spin-orbitals φ_i satisfy the eigenvalue equations

$$[F(i) + \lambda v(i)]\, \varphi_i(i) = \omega_i\, \varphi_i(i), \quad (i = 1, \cdots 2n) \tag{3.3}$$

where

$$F(i) = -\tfrac{1}{2}\nabla_i^2 - \sum_\alpha \frac{Z_\alpha}{r_{\alpha i}} + \sum_{j=1}^{2n} [J_j(i) - K_j(i)] \tag{3.4}$$

$J_j(i)$ and $K_j(i)$ being defined by

$$J_j(i) = \int \frac{|\varphi_j(j)|^2}{r_{ij}} d\tau_j \tag{3.5}$$

$$K_j(i)\varphi_k(i) = \int \frac{\varphi_j^*(j)\varphi_k(j)}{r_{ij}} d\tau_j \, \varphi_j(i) \,. \tag{3.6}$$

If we substitute

$$\varphi_i = \phi_i + \lambda \varphi_i^{(1)} + \lambda^2 \varphi_i^{(2)} + \cdots \tag{3.7}$$

and

$$w_i = w_i^{(0)} + \lambda w_i^{(1)} + \lambda^2 w_i^{(2)} + \cdots \tag{3.8}$$

into Eq. (3.3), the equations for various orders are obtained by equating equal powers of λ . Thus, the zeroth-order equation defines the orthonormal set of unperturbed functions ϕ_i ,

$$(F_0(i) - w_i^{(0)})\,\phi_i(i) = 0, \quad (i = 1, \cdots, 2n) \tag{3.9}$$

where

$$F_0(i) = -\frac{1}{2}\nabla_i^2 - \sum_\alpha \frac{Z_\alpha}{r_{\alpha i}} + \sum_{j=1}^{2n} \left[J_j^0(i) - K_j^0(i)\right] \tag{3.10}$$

$J_j^0(i)$ and $K_j^0(i)$ being defined by

$$J_j^0(i) = \int \frac{|\phi_j(i)|^2}{r_{ij}} d\tau_j \tag{3.11}$$

$$K_j^0(i)\,\phi_k(i) = \int \frac{\phi_j^*(j)\,\phi_k(j)}{r_{ij}} d\tau_j\,\phi_j(i) \,. \tag{3.12}$$

The total unperturbed wavefunction is

$$\Psi^{(0)} = \mathcal{A} \prod_{i=1}^{2n} \phi_i(i) \tag{3.13}$$

and satisfies the equation

$$H_0 \Psi^{(0)} = W^{(0)} \Psi^{(0)} \tag{3.14}$$

where

$$H_0 = \sum_{i=1}^{2n} F_0(i) - \sum_{i<j}^{2n} \left(J_{ij}^0 - K_{ij}^0 \right) \tag{3.15}$$

J_{ij}^0 and K_{ij}^0 being given by

$$J_{ij}^0 = \int \frac{|\phi_i(i)|^2\,|\phi_j(j)|^2}{r_{ij}} d\tau_j\, d\tau_i \tag{3.16}$$

$$K_{ij}^0 = \int \frac{\phi_i^*(i)\,\phi_j(i)\,\phi_j^*(j)\,\phi_i(j)}{r_{ij}} d\tau_j\, d\tau_i \tag{3.17}$$

and $W^{(0)}$ is the unperturbed Hartree-Fock energy,

$$W^{(0)} = \sum_{i=1}^{2n} w_i^{(0)} - \sum_{i<j}^{2n} \left(J_{ij}^{0} - K_{ij}^{0} \right) . \tag{3.18}$$

The first-order equation determines $\varphi_i^{(1)}$;

$$\left(F_0(i) - w_i^{(0)} \right) \varphi_i^{(1)} + \left(v - w_i^{(1)} \right) \phi_i = - \sum_{j=1}^{2n} \left[J_j'(i) - K_j'(i) \right] \tag{3.19}$$

where $J_j'(i)$ and $K_j'(i)$ take the forms

$$J_j'(i) = \int \frac{\varphi_j^{(1)*}(j)\,\phi_j(j) + \varphi_j^{(1)}(j)\,\phi_j^{*}(j)}{r_{ij}}\, d\tau_j \tag{3.20}$$

$$K_j'(i)\phi_k(i) = \int \frac{\phi_j^{*}(j)\phi_k(j)}{r_{ij}} d\tau_j\, \varphi_j^{(1)}(i) + \int \frac{\varphi_j^{(1)*}(j)\,\phi_k(j)}{r_{ij}} d\tau_j\, \phi_j(i) . \tag{3.21}$$

From Eqs. (3.9) and (3.19), $w_i^{(1)}$ are determined;

$$w_i^{(1)} = \langle \phi_i, v\phi_i \rangle + \sum_{j=1}^{2n} \left[\int J_j' \phi_i^{*} \phi_i \, d\tau_i - \int \phi_i^{*} K_j' \phi_i \, d\tau_i \right] . \tag{3.22}$$

Similarly $w_i^{(2)}$ are obtained from Eqs. (3.9), (3.19) and the second-order equation. (See reference 10). The total first- and second-order energies are given by†

† Dalgarno's[9,10] expression for $W^{(2)}$ includes $-\sum_i \sum_j \langle \phi_j, v\phi_i \rangle \langle \varphi_i^{(1)}, \phi_j \rangle$. Those terms, however, vanish since $\langle \varphi_i, \varphi_j \rangle = \delta_{ij}$ leads to $\langle \phi_i, \varphi_j^{(1)} \rangle + \langle \varphi_i^{(1)}, \phi_j \rangle = 0$.

$$W^{(1)} = \sum_{i=1}^{2n} \langle \phi_i, v\phi_i \rangle \tag{3.23}$$

$$W^{(2)} = \sum_{i=1}^{2n} \langle \phi_i, v\phi_i^{(1)} \rangle . \tag{3.24}$$

The perturbed orbitals in Eqs. (3.19) are coupled together both by direct and exchange interactions, and consequently the equations are awkward to solve. This coupled approximation has so far only been applied rigorously to the evaluation of the polarizabilities and shielding factors for the He[10,11,13] and Be[14] sequences, but with very encouraging results.

2. The uncoupled Hartree-Fock approximation.

The difficulty in solving Eqs. (3.19) is due to the coupling terms which arise from the demand for self-consistency in the presence of the perturbation V. A simpler set of equations for the first-order wavefunction can be obtained by neglecting the effect of the perturbation on the Hartree-Fock potential.[10] The perturbed equation for this so-called uncoupled Hartree-Fock approximation is then

$$(H_0 + \lambda V - W)\Psi = 0, \tag{3.25}$$

where H_0 is the Hartree-Fock Hamiltonian for the unperturbed system, given by Eq. (3.15). There are two methods for obtaining the first-order perturbation equations for the one-electron first-order function $\varphi_i^{(1)}$, corresponding to Eqs. (3.19) for the coupled approximation. These methods lead to different equations, but in spite of this the relation between them has not been clarified in the literature. The difference between the methods depe nds on whether Eq. (3.25) is first separated into one-electron equations, to which perturbation theory is then applied (method A); or whether the perturbation theory is first applied to Eq. (3.25), and the resulting first-order many-electron equation is then separated into one-electron equations (method B). Both methods lead to the same results provided the perturbation equations are solved exactly. Method A is considerably simpler than method B, and is therefore to be preferred when no further approximations are involved. On the other hand, if the equations cannot be solved analytically, and a variational approximation is being sought, the variational form of method B is appropriate. The essential difference is that the equations of method A assume that the different perturbed orbitals are orthogonal, whereas this is not assumed in method B.

Method A

The perturbed Hamiltonian $H_0 + \lambda V$ occuring in Eq. (3.25) is a sum of one-electron operaters, and may be written in the form

$$\sum_i \left[F_0(i) + \lambda v(i) \right] \Psi = W' \Psi \qquad (3.26)$$

where

$$W' = W - \sum_{i<j} \left(J_{ij}^{0} - K_{ij}^{0} \right) \tag{3.27}$$

and the total perturbed wavefunction Ψ must have the determinantal form

$$\Psi = \mathcal{A} \prod_{i=1}^{2n} \varphi_i(i) \, . \tag{3.28}$$

The many-electron equation (3.26) can be separated into one-electron equations which are uncoupled, provided that the orbitals φ_i are orthogonal to one another. This leads to the equations

$$(F_0 + \lambda V - w_i)\varphi_i = 0, \quad (i = 1, \cdots, 2n) \tag{3.29}$$

which are analogous to Eqs. (3.3) for the coupled approximation. Eqs. (3.29) are consistent with the assumption of orthogonal orbitals, since it follows directly that $\langle \varphi_i, \varphi_j \rangle = 0$ if $w_i \neq w_j$, or if φ_i and φ_j have opposite spin, and indeed, even in the case of degeneracy which is not split by V , it is always possible to choose the orbitals so that

$$\langle \varphi_i, \varphi_j \rangle = \delta_{ij} \tag{3.30}$$

The perturbation treatment of Eqs. (3.29) is similar to that of Eqs. (3.3),

but simpler. The first-order equation is

$$(F_0 - w_i^{(0)})\varphi_i^{(1)} + (v - w_i^{(1)})\phi_i = 0 \ , \tag{3.31}$$

where $\phi_i \equiv \varphi_i^{(0)}$ and $w_i^{(1)} = \langle \phi_i, v\phi_i \rangle$.
The total second-order energy is

$$W^{(2)} = \sum_{i=1}^{2n} w_i^{(2)}$$
$$= \sum_{i=1}^{2n} \langle \phi_i, v\varphi_i^{(1)} \rangle \ , \tag{3.32}$$

which is of the same form as Eq. (3.24). Note that it follows from Eq. (3.30) that orthogonality of φ_i and φ_j through first order in λ require that

$$\langle \varphi_i^{(1)}, \phi_j \rangle + \langle \phi_i, \varphi_j^{(1)} \rangle = 0. \tag{3.33}$$

This condition can be easily seen to follow from Eq. (3.31), and in particular

$$\langle \phi_j, \varphi_i^{(1)} \rangle = \frac{\langle \phi_j, v\phi_i \rangle}{w_i^{(0)} - w_j^{(0)}} \ , \ i \neq j \ . \tag{3.34}$$

Method B

In this method[10,15] the many-electron Schrödinger equation (3.25) is first of all expanded in powers of λ . The zeroth-order equation is the unperturbed Hartree-Fock equation (3.14). The first-order perturbation equation is

$$(H_0 - W^{(0)})\Psi^{(1)} + (V - W^{(1)})\Psi^{(0)} = 0 \qquad (3.35)$$

where V is the sum of one-electron perturbation, Eq. (3.2). We are interested in solutions of Eq. (3.35) which have the antisymmetrized form, derivable from Eq. (3.28),

$$\Psi^{(1)} = \sum_{i=1}^{2n} \mathcal{A} \prod_{j\neq i}^{2n} \phi_j(j)\,\varphi_i^{(1)}(i) \qquad (3.36)$$

Eq. (3.35) may be separated into one-electron equations by the following procedure: Substitute Eq. (3.36) into Eq. (3.35), multiply by all $\phi_k^*(k)$ except $\phi_i^*(i)$, and integrate over all electronic coordinates except of electron i. The result is

$$(F_0 - w_i^{(0)})\varphi_i^{(1)} + (v - w_i^{(1)})\phi_i = \sum_{j\neq i}^{2n} \{(w_j^{(0)} - w_i^{(0)})\langle \phi_j, \varphi_i^{(1)}\rangle + \langle \phi_j, v\phi_i\rangle\}\phi_j \qquad (3.37)$$

The cross terms on the right hand side of Eq. (3.37) arise from the determinental form of Ψ, and can therefore be described as exchange terms.[15] They guarantee the consistency of the equations irrespective of the value of the integral $\langle \phi_j, \varphi_i^{(1)}\rangle$, as can be seen by multiplying Eq. (3.37) by ϕ_j^* and integrating.

Clearly the solutions $\varphi_i^{(1)}$ of Eq. (3.37) may not be identical with those of Eq. (3.31) derived by method A. Thus, it is easily seen that

$$\varphi_i^{(1)}[\text{Eq. (3.37)}] = \varphi_i^{(1)}[\text{Eq. (3.31)}] + \sum_{j\neq i}^{2n} C_{ij}\,\phi_j \qquad (3.38)$$

where the coefficients C_{ij} are arbitrary. However, the total first-order wavefunction $\Psi^{(1)}$, given by Eq. (3.36), is essentially independent of the coefficients C_{ij}, and two methods therefore give the same results. The second-order energy is given by

$$W^{(2)} = \langle \Psi^{(1)}, V\Psi^{(0)} \rangle = \sum_{i=1}^{2n} \left\{ \langle \varphi_i^{(1)}, V\phi_i \rangle - \sum_{j\neq i}^{2n} \langle \phi_j, V\phi_i \rangle \langle \varphi_i^{(1)}, \phi_j \rangle \right\}. \qquad (3.39)$$

It is easily seen that $W^{(2)}$ is also independent of the value of the coefficients C_{ij}. If the orthogonality condition (3.33) is satisfied, the double summation vanish, and Eq. (3.23) for $W^{(2)}$ is recovered.

Method A is analogous to the procedure used to derive the equations of the coupled Hartree-Fock approximation, discussed in Section III.1. Methods A and B are equivalent, but since Eqs. (3.31) and (3.32) of method A are simpler than Eqs. (3.37) and (3.39) of method B, method A is clearly to be preferred when no further approximation is contemplated.

Hylleraas variational principle

For most molecular systems it is not possible to solve the first-order perturbation equation (3.31) analytically. However, variational

approximations to $\Psi^{(1)}$ and $W^{(2)}$ can be found by using the Hylleraas variational principle.[10,15] This principle can be applied either to the total first-order perturbation equation (3.35) or individually to the equations (3.31) for the one-electron first-order functions $\varphi_i^{(1)}$.

The application to the many-electron equation (3.35) is straightforward. For the ground state of the system, the functional

$$\tilde{W}^{(2)} = \langle \tilde{\Psi}^{(1)}, (H_0 - W^{(0)})\tilde{\Psi}^{(1)} \rangle + \langle \tilde{\Psi}^{(1)}, (V - W^{(1)})\Psi^{(0)} \rangle + \langle \Psi^{(0)}, (V - W^{(1)})\tilde{\Psi}^{(1)} \rangle \tag{3.40}$$

is an upper bound to the exact second-order energy $W^{(2)}$. The first-order trial function $\tilde{\Psi}^{(1)}$ must have the same form as the exact function $\Psi^{(1)}$, given by Eq. (3.36), namely

$$\tilde{\Psi}^{(1)} = \sum_{i=1}^{2n} \mathcal{A} \prod_{j \neq i} \phi_j(j)\, \tilde{\varphi}_i^{(1)}(i) \quad . \tag{3.41}$$

When Eq. (3.41) is substituted into Eq. (3.40), it may be reduced to a sum of one-electron functionals,

$$\tilde{W}^{(2)} = \sum_{i=1}^{2n} \tilde{w}_i^{(2)} \tag{3.42}$$

where

$$\tilde{w}_i^{(2)} = \langle \tilde{\varphi}_i^{(1)}, (F_0 - w_i^{(0)})\tilde{\varphi}_i^{(1)} \rangle + \langle \tilde{\varphi}_i^{(1)}, (v - w_i^{(1)})\phi_i \rangle + \langle \phi_i, (v - w_i^{(1)})\tilde{\varphi}_i^{(1)} \rangle - \sum_{j \neq i}^{2n} \{ (w_j^{(0)} - w_i^{(0)}) |\langle \tilde{\varphi}_i^{(1)}, \phi_j \rangle|^2 + \langle \tilde{\varphi}_i^{(1)}, \phi_j \rangle \langle \phi_j, v\phi_i \rangle + \langle \phi_i, v\phi_j \rangle \langle \phi_j, \tilde{\varphi}_i^{(1)} \rangle \} . \tag{3.43}$$

The minimization of $\widetilde{W}^{(2)}$ with respect to variations in the trial functions $\widetilde{\varphi}^{(1)}$ is therefore equivalent to the minimization of the individual one-electron functionals $\widetilde{w}_i^{(2)}$. The functional $\widetilde{w}_i^{(2)}$ of Eq. (3.43) is an upper bound to the exact expression

$$w_i^{(2)} = \langle \phi_i , \varphi_i^{(1)} \rangle - \sum_{j\neq i}^{2n} \langle \phi_i, v\phi_j \rangle \langle \phi_j, \varphi_i^{(1)} \rangle \tag{3.44}$$

where $\varphi_i^{(1)}$ satisfies Eq. (3.37). In fact, if $\widetilde{\varphi}_i^{(1)} = \varphi_i^{(1)} + \delta\varphi_i^{(1)}$, then

$$\widetilde{w}_i^{(2)} - w_i^{(2)} = \langle Q\,\delta\widetilde{\varphi}_i^{(1)}, (F_0 - w_i^{(0)})\, Q\,\delta\widetilde{\varphi}_i^{(1)} \rangle \geq 0 \tag{3.45}$$

where

$$Q = 1 - \sum_{j=1}^{2n} |\phi_j\rangle\langle\phi_j|$$

projects out all occupied zeroth-order spin-orbitals.

The minimization of $\widetilde{w}_i^{(2)}$ with respect to arbitrary variation $\widetilde{\varphi}_i^{(1)}$ leads automatically to the first-order perturbation equations (3.37) of method B since the orthogonality conditions (3.33) are not assumed in the trial function $\widetilde{\Psi}^{(1)}$ of Eq. (3.41). If they are assumed,† then as pointed out above, Eq. (3.37) can be replaced by Eq. (3.31).

An alternative variational procedure could be based on the simpler one-electron functionals suggested by the equations of method A

† The sufficient condition for the orthogonality relations (3.33) to be valid for trial functions $\widetilde{\varphi}_i^{(1)}$, and therefore for Eq. (3.37) to reduce to Eq. (3.31), is that $\delta\widetilde{\varphi}^{(1)} = \gamma\phi_j$ (all $j\neq i$) are allowed variations.[8]

[Eq. (3.37)], namely

$$\tilde{w}_i^{(2)} = \langle \tilde{\varphi}_i^{(1)}, (F_0 - w_i^{(0)})\, \tilde{\varphi}_i^{(1)} \rangle + \langle \tilde{\varphi}_i^{(1)}, (v - w_i^{(1)})\, \phi_i \rangle + \langle \phi_i, (v - w_i^{(1)})\, \tilde{\varphi}_i^{(1)} \rangle . \tag{3.46}$$

However, these functionals are not upper bounds to the exact second-order energies $w_i^{(2)}$ (except for the lowest one-electron level), and hence it is necessary to impose the orthogonality conditions, Eq. (3.33), on the trial functions, namely

$$\langle \tilde{\varphi}_i^{(1)}, \phi_j \rangle + \langle \phi_i, \tilde{\varphi}_j^{(1)} \rangle = 0, \quad (\text{all } i, j) . \tag{3.47}$$

The procedure of making the $\tilde{w}_i^{(2)}$ of Eq. (3.46) stationary with respect to the $\tilde{\varphi}_i^{(1)}$, subject to the constraints, Eq. (3.47), is completely equivalent to that based on the functional, Eq. (3.43). For arbitrary variations $\delta\tilde{\varphi}_i^{(1)}$, the Lagrange multipliers associated with the constraints lead to the cross terms on the right hand side of Eq. (3.37). It is interesting to note the relationship between the variational procedure discussed here for the individual electrons, and that proposed by Sinanoglu[8, 16] for excited states of a system.

Karplus-Kolker approximation

The evaluation of the first-term of Eq. (3.43) is complicated by the presence of the non-local exchange potential in F_0, which gives rise to two-electron integrals. Karplus and Kolker[15] neglect these terms for the sake of simplicity. Here we briefly discuss the

approximation involved.

If we substitute

$$\tilde{\varphi}_i^{(1)} = \phi_i \tilde{f}_i \tag{3.48}$$

into Eq. (3.43), the first term can be written as

$$\langle \tilde{\varphi}_i^{(1)}, (F_0 - \omega_i^{(0)}) \tilde{\varphi}_i^{(1)} \rangle = \langle \phi_i \tilde{f}_i , [F_0, \tilde{f}_i] \phi_i \rangle \ , \tag{3.49}$$

where the square brackets denote a commutator. By substituting Eq. (3.10) into Eq. (3.49), we obtain

$$\begin{aligned} &\langle \tilde{\varphi}_i^{(1)}, (F_0 - \omega_i^{(0)}) \tilde{\varphi}_i^{(1)} \rangle \\ &= -\tfrac{1}{2} \langle \phi_i \tilde{f}_i , [\nabla^2, \tilde{f}_i] \phi_i \rangle - \sum_{j=1}^{2n} \langle \phi_i \tilde{f}_i , [K_j^0, \tilde{f}_i] \phi_i \rangle \end{aligned} \tag{3.50}$$

where K_j^0 is a non-local exchange contribution to the potential defined by Eq. (3.12). The second summation term in Eq. (3.50) is the one neglected by Karplus and Kolker.[15] It would clearly vanish if K_j^0 were a local potential. The explicit form of the jth term in the sum is

$$\begin{aligned} \langle \phi_i \tilde{f}_i, [K_j^0, \tilde{f}_i] \phi_i \rangle &= \int d\tau_1 \, \phi_i^*(1) \tilde{f}_i^*(1) \phi_j(1) \int d\tau_2 \, \frac{\phi_j^*(2) \tilde{f}_i(2) \phi_i(2)}{r_{12}} \\ &- \int d\tau_1 \, \phi_i^*(1) \tilde{f}_i^*(1) \tilde{f}_i(1) \phi_j(1) \int d\tau_2 \, \frac{\phi_j^*(2) \phi_i(2)}{r_{12}} \ . \end{aligned} \tag{3.51}$$

This difference may be small in some cases, even though K_j^0 itself is not negligible. If the Hartree-Fock potential in F_0 is replaced by the so-called Sternheimer potential,[17] which is local, then the two-electron terms (3.51) do not appear. However, the Karplus-Kolker approximation does not imply the use of the Sternheimer potential, or the neglect of K_j^0, but simply that the integrals in Eq. (3.51) cancel each other approximately.

Using this approximation, the first term in Eq. (3.43) can be written in the form

$$\langle \tilde{\varphi}_i^{(1)}, (F_0 - w_i^{(0)})\tilde{\varphi}_i^{(1)} \rangle = -\frac{1}{2}\langle \phi_i \tilde{f}_i, [\nabla^2, \tilde{f}_i]\phi_i \rangle$$
$$= \frac{1}{2}\langle \phi_i, |\nabla \tilde{f}_i|^2 \phi_i \rangle \tag{3.52}$$

where the commutator has been reduced by a well-known procedure.[8] By substituting Eqs. (3.48) and (3.52) into Eq. (3.43), we have

$$\tilde{w}_i^{(2)} = \frac{1}{2}\langle \phi_i, |\nabla \tilde{f}_i|^2 \phi_i \rangle + \langle \phi_i, (v - w_i^{(1)})(\tilde{f}_i^* + \tilde{f}_i)\phi_i \rangle$$
$$- \sum_{j\neq i}^{2n} \left\{ (w_j^{(0)} - w_i^{(0)}) |\langle \phi_i, \tilde{f}_i \phi_i \rangle|^2 + \langle \phi_i, (\tilde{f}_i^* + \tilde{f}_i)\phi_j \rangle \langle \phi_j, v\phi_i \rangle \right\}. \tag{3.53}$$

This equation only involves one-electron integrals.

Most of the previous calculations of second-order perturbations are closely related to the uncoupled Hartree-Fock approximation. The dipole and quadrupole polarizabilities and shielding factors for the helium isoelectronic sequence have been obtained by numerical integration[17] of the first-order equation and by variational methods.[18]

For beryllium the solutions of Eq. (3.37) for dipole and quadrupole perturbations have been obtained by Dalgarno and McNamee.[19] The variational method using Eq. (3.53) has been employed for the calculations of magnetic susceptibility of diatomic molecules by Karplus and Kolker[15] and atomic dipole polarizabilities by Yoshimine and Hurst.[20]

3. Accuracy in the Hartree-Fock approximation

To examine the error involved, one can consider the effect of the change in the unperturbed Hartree-Fock wavefunction $\Psi^{(0)}$ produced by applying a perturbation which is the difference between the Hartree-Fock Hamiltonian and the actual Hamiltonian of the system. Thus it has been shown by Dalgarno[10] that in the fully coupled approximation the second-order energy is correct through the first order in the error of the unperturbed Hamiltonian, whereas for the second-order energy derived from the uncoupled approximation there is a non-vanishing first-order correction. Hence coupled approximation should lead to much more accurate results than the uncoupled approximation. If we employ Eq. (3.53) to solve the perturbation equation by the variational method further sacrifice in accuracy is clearly made. In the evaluation of the matrix element $\langle \tilde{\varphi}_i^{(1)}, (F_0 - w_i^{(0)}) \tilde{\varphi}_i^{(1)} \rangle$ the terms which arise from the nonlocal exchange potential in F_0 are neglected, and in this way the difficulty of evaluating two-electron integrals can be avoided.

In considering the practical approximation further introduction of error has to be recognized. Since the analytical Hartree-Fock orbitals are obtained in general by expanding the one-electron

rbitals in terms of a finite set, the resulting $\Psi^{(0)}$ is no longer the exact Hartree-Fock solution to the problem. Thus first-order errors in the second-order energy $W^{(2)}$ are introduced, even for the coupled approximation, by the lack of completeness of the basis set. Furthermore, it should be noticed that, as Epstein has pointed out, if one uses an approximate ground state wavefunction in the variational principle for the second-order energy the approximate energy need have no special relationship to the exact energy (it may be larger or smaller).[21] One obtains a less well controlled approximation to the exact second-order energy.[22] However, for a good analytic approximation to the ground state Hartree-Fock function, the first-order corrections to the second-order energy may be expected to be small, and we may obtain a sufficiently well controlled approximation to the exact second-order energy.

4. Variational solution of perturbation equation

An approximate variational solution of Eq. (3.37) may be obtained by minimizing the functional $\widetilde{W}_i^{(2)}$ given by Eq. (3.53). We put

$$\widetilde{f}_i = \sum_{k=1}^{r} a_{ik} u_k \tag{3.54}$$

where u_k are a finite (real) basis set, and a_{ik} are linear variational parameters. By introducing Eq. (3.54) into Eq. (3.53) the condition $\delta \widetilde{W}_i^{(2)} = 0$ is equivalent to requiring

$$\frac{\partial \tilde{w}_i^{(2)}}{\partial a_{ik}} = 0 , \quad k = 1, \cdots, r . \tag{3.55}$$

These conditions lead to the set of simultaneous linear inhomogeneous equations

$$\sum_m A_{im}^k a_{im} = -2 B_i^k \tag{3.56}$$

where

$$A_{im}^k = \langle \phi_i , (\vec{\nabla} u_k \cdot \vec{\nabla} u_m) \phi_i \rangle - \sum_{j \neq i}^{2n} (w_j^{(0)} - w_i^{(0)}) \langle \phi_j , u_k \phi_i \rangle \langle \phi_i , u_m \phi_j \rangle \tag{3.57}$$

$$B_i^k = \langle \phi_i , v u_k \phi_i \rangle - \sum_{j \neq i}^{2n} \langle \phi_j , v \phi_i \rangle \langle \phi_i , u_k \phi_j \rangle . \tag{3.58}$$

The coefficients a_{ik} are found for each orbital by solving the set of Eq. (3.56). Once those coefficients are obtained the contribution to the second-order energy from ith spin-orbital $w_i^{(2)}$ [Eq. (3.38)] is given by

$$w_i^{(2)} = \sum_k a_{ik} B_i^k \tag{3.59}$$

where β_i^k are given by Eq. (3.58). The total second-order energy is obtained by summing the contribution of each spin-orbital.

5. Dipole moment expression

In the Hartree-Fock approximation the leading term of the dipole moment of a heteronuclear molecule AB may be written as [cf. Eq. (2.21)]

$$\langle \mu \rangle = \lambda \left[Z_0 R + 2 \langle \Psi^{(1)}, \mu \Psi^{(0)} \rangle \right] \tag{3.60}$$

where $\Psi^{(0)}$ is the unperturbed Hartree-Fock function, Eq. (3.13), and $\Psi^{(1)}$ is given by Eq. (3.36). By substituting Eqs. (3.13), (2.20) and (3.36) into Eq. (3.60), we obtain

$$\langle \mu \rangle = \lambda \left[Z_0 R + 2 \sum_{i=1}^{2n} \mu_i^{(1)} \right] \tag{3.61}$$

where

$$\mu_i^{(1)} = - \langle \phi_i, z \varphi_i^{(1)} \rangle + \sum_{j \neq i}^{2n} \langle \phi_i, z \phi_j \rangle \langle \phi_j, \varphi_i^{(1)} \rangle . \tag{3.62}$$

If we intoduce the variational solution of the first-order function $\tilde{\varphi}^{(1)} = \phi_i \tilde{f}_i$ where $\tilde{f}_i$ has the form of Eq. (3.54), Eq. (3.62) becomes

$$\mu_i^{(1)} = \sum_k a_{ik} D_i^k \tag{3.63}$$

where

$$D_i^k = -\langle \phi_i, z u_k \phi_i \rangle + \sum_{j \neq i}^{2n} \langle \phi_i, z \phi_j \rangle \langle \phi_j, u_k \phi_i \rangle . \tag{3.64}$$

Hence the dipole moment may be approximated by the following formula

$$\langle \mu \rangle = \lambda \left[Z_0 R + 2 \sum_{i=1}^{2n} \sum_{k=1}^{\ell} a_{ik} D_i^k \right] . \tag{3.65}$$

Note that, if the orthogonality condition (3.47) is satisfied, Eq. (3.65) reduces to

$$\langle \mu \rangle = \lambda \left[Z_0 R - 2 \sum_{i=1}^{2n} \sum_{k=1}^{\ell} a_{ik} \langle \phi_i, z u_k \phi_i \rangle \right] . \tag{3.66}$$

IV TREATMENT OF CO BASED ON N_2

1. Electronic potential energy curves

Let $\Psi_1^{(0)}$ and $W_1^{(0)}$ be the wave function and the electronic energy for the lowest $^1\Sigma_g^+$ state of N_2 which dissociates to N atoms in ground ^4S states, and $\Psi_2^{(0)}$ and $W_2^{(0)}$ be those for the $^1\Sigma_g^+$ state of N_2 which dissociates to the ions, N^+ and N^-, in ground ^3P states. Then using ionization potential[23] and electron affinity[24] of N atom, we obtain

$$\begin{aligned} W_2^{(0)}(\infty) - W_1^{(0)}(\infty) &= (\text{I.P. of } N) - (\text{E.A. of } N) \\ &= (14.54 - 0.05)\ ev \\ &= 14.49\ ev \\ &= 0.5325\ H \end{aligned} \tag{4.1}$$

Similarly let Ψ_1 and W_1 be the wave function and the electronic energy of the lowest $^1\Sigma^+$ state of CO which dissociates to atoms C and O in ^3P states, and Ψ_2 and W_2 be those for the $^1\Sigma^+$ state which dissociates to ions C^- and O^+ in ^4S states. Then using ionization potential[23] of O atom, and electron affinity[24] of C atom we obtain

$$\begin{aligned} W_2(\infty) - W_1(\infty) &= (\text{I.P. of } O) - (\text{E.A. of } C) \\ &= (13.61 - 1.12)\ ev \\ &= 12.49\ ev \\ &= 0.4590\ H \end{aligned} \tag{4.2}$$

Making use of the electronic energies of N, C^- and O^+ which are computed from ionization potentials given in Moore,[23] the energy difference of $2N - (C^- + O^+)$ is given by

$$
\begin{aligned}
&W_1^{(0)}(\infty) - W_2(\infty) \\
&= \{(\text{I. Ps. of } O^+) + (\text{I. Ps. of } C) + (\text{E. A. of } C)\} - 2(\text{I. Ps. of } N) \\
&= \{2029.66 + 1029.81 + 1.12\} - 2 \cdot 1485.65 \quad \text{ev} \\
&= 89.29 \text{ ev} \\
&= 3.281 \text{ H} \quad .
\end{aligned}
\tag{4.3}
$$

This is to be compared with the value calculated by Eq. (2.34),

$$
W_1^{(0)}(\infty) - W_2(\infty) \simeq \sum_{i=1}^{7} \frac{1}{n_i^2} = 3.250 \text{ H} \tag{4.4}
$$

which agrees well with the empirical value [Eq. (4.3)] .

The calculation of the energy difference between C + O atoms and N + N atoms (ground states) using $1/Z$-expansion method is given in Appendix. The result, $W_1^{(0)}(\infty) - W_1(\infty) \simeq 2.85$ H is compared with the empirical value, 3.74 H, which is computed using ionization potential[23] of each electron of N, C and O atoms. The less agreement shows that the higher order terms should be included in $1/Z$-expansions of the electronic energies of atoms.

The electronic energies against the internuclear separation R are shown schematically in Fig. 2.

2. Schwartz discriminant

The object of this section is to check the inequality Eq. (2.27b) which is a check on the validity of taking the leading terms in the expansion of the electronic energy difference, $W - W^{(0)}$, and the dipole moment, $\langle \mu \rangle$. To find $\Delta W(R_0) = W_1(R_0) - W_1^{(0)}(R_0)$ where R_0 is the equilibrium internuclear distance of N_2, we expand the molecular energy of CO, $E_1(R)$, which is the sum of the electronic energy and the internuclear repulsion energy, about the equilibrium internuclear distance, R_e

$$E_1(R) = E_1(R_e) + \frac{1}{2}(R-R_e)^2\left(\frac{d^2E_1}{dR^2}\right)_e + \cdots \tag{4.5}$$

where $(d^2E_1/dR^2)_e = k_e$ is the force constant for CO. Also we note that

$$E_1^{(0)}(R_0) = -D_1^{(0)} + E_1^{(0)}(\infty)$$
$$E_1(R_e) = -D_1 + E_1(\infty) \tag{4.6}$$

where $D_1^{(0)}$ and D_1 are the dissociation energies of N_2 and CO. using Eqs. (4.5) and (4.6), we obtain

$$\Delta W(R_0) \simeq (D_1 - D_1^{(0)}) + \{E_1^{(0)}(\infty) - E_1(\infty)\} + (Z_C Z_O - Z_N^2)/R_0 + (R_0 - R_e)^2 k_e/2 \tag{4.7}$$

where Z_N , Z_C and Z_O are the nuclear charges of N, C and O. By making use of the necessary molecular constants given in Table I, we obatin

$$\Delta W(R_0) = -3.313\ H. \tag{4.8}$$

Also using $\langle\mu\rangle = -0.15$ Debye[4] and $\alpha = 23.8 \times 10^{-25} cm^3$,[25] we get

$$(\lambda Z_N R_0 - \langle\mu\rangle)^2/(2\alpha) = 0.126\ H. \tag{4.9}$$

Thus the inequality (2.27b) becomes $3.313 \geqslant 0.126$, and therefore easily confirmed for the case of N_2 and CO. The use of the leading terms in the perturbation expansions is therefore not in conflict with the Schwartz inequality.

3. Correlation of the electronic states and degeneracy

The proposed perturbation treatment in Section II expands the wavefunction Ψ_1 and energy $W_1(R)$ for the lowest state of CO about those for the lowest state of N_2, namely $\Psi_1^{(0)}$ and $W_1^{(0)}(R)$, in powers of $\lambda = (Z_A - Z_B)/(Z_A + Z_B) = 1/7$. The expansions are given in Eqs. (2.5) and (2.6). However, the treatment in Section II overlooks the following difficulty: The electronic states of CO and N_2 which are related by the perturbation theory must be "adiabatically correlated" in the sense that if λ were reduced from 1/7 to 0 the states must become identical.

When the atoms are separated at $R = \infty$ we know that in fact the state $C + O$ is correlated with $N^+ + N^-$, and the state $N + N$ is correlated with $C^- + O^+$. That is:

$$\lim_{\lambda \to 0} \lim_{R \to \infty} \Psi_1 = \Psi_2^{(0)} \tag{4.10}$$

although

$$\lim_{\substack{\lambda \to 0 \\ (R \neq \infty)}} \Psi_1 = \Psi_1^{(0)} \quad . \tag{4.11}$$

When $R = 0$ at the united atom (Si) the energies are independent of λ since the nuclei are united and only the total charge $\Sigma\ (=14)$ matters. The correlations of the states are shown schematically in Figs. 3a, 3b, and 3c.

Now to check the applicability of the proposed perturbation theory, we consider the crossing point of two states. When R is the order of the equilibrium internuclear seperation of N_2, R_0 , we approximate two states of CO as follows:

$$\Psi_1(1) = \Psi_1^{(0)} + \lambda \Psi_1^{(1)}$$

$$\Psi_2(1) = \Psi_2^{(0)} + \lambda \Psi_2^{(1)} \tag{4.12}$$

where $\Psi_1^{(1)}$ and $\Psi_2^{(1)}$ are the solutions of the first-order perturbation equations

$$(\mathcal{H}_0 - E_i^{(0)})\,\Psi_i^{(1)} + V\,\Psi_i^{(0)} = 0 \quad , \quad i = 1, 2. \tag{4.13}$$

Then since $W_1^{(1)} = W_2^{(1)} = 0$ and $W_1^{(3)} = W_2^{(3)} = 0$ due to u-symmetry of V, we have

$$W_1(1) = W_1^{(0)} + \frac{\lambda^2 W_1^{(2)}}{1 + \lambda^2 S_1} \tag{4.14a}$$

$$W_2(1) = W_2^{(0)} + \frac{\lambda^2 W_2^{(2)}}{1 + \lambda^2 S_2} \tag{4.14b}$$

where $S_1 = \langle \Psi_1^{(1)}, \Psi_1^{(1)} \rangle$ and $S_2 = \langle \Psi_2^{(1)}, \Psi_2^{(1)} \rangle$. If we put $W_1(1) = W_2(1)$ and neglect λ^2 terms in denominators, we obtain the approximate crossing point λ_c

$$\lambda_c = \sqrt{-\frac{\Delta W^{(0)}}{\Delta W^{(2)}}} \tag{4.15}$$

where $\Delta W^{(0)} = W_2^{(0)} - W_1^{(0)}$ and $\Delta W^{(2)} = W_2^{(2)} - W_1^{(2)}$. It is noticed that λ_c is real only if $\Delta W^{(0)}\,\Delta W^{(2)} < 0$, and we may assume $\lambda_c \gg 1/7$ since it appears to be $|\Delta W^{(0)}| \gg |\Delta W^{(2)}|$. (See Fig. 4a).

At the limit as $R \rightarrow \infty$ the separated ions N^+ and N^- are in different ground ^3P states and there exist four $^1\Sigma^+$ states[26] which have equal energies without the perturbation V and interact each other with the perturbation V. Hence for $N^+ + N^-$ at $R = \infty$, the degenerate perturbation theory should be applied. Suppose that four $^1\Sigma^+$ states of $N^+ + N^-$ can be described by the orthonormal wave functions $\phi_1(a,b)$, $\phi_1(b.a)$, $\phi_2(a,b)$ and $\phi_2(b,a)$ where $\phi_1(b,a)$ and $\phi_2(b,a)$ are obtained from $\phi_1(a.b)$ and $\phi_2(a,b)$ by interchanging nitrogen nuclei A and B. From these four wave functions, we can construct two symmetric wave functions and two antisymmetric wave functions;

$$\begin{aligned}
\psi_{1g} &= \frac{1}{\sqrt{2}}\{\phi_1(a,b) + \phi_1(b,a)\} \\
\psi_{2g} &= \frac{1}{\sqrt{2}}\{\phi_2(a,b) + \phi_2(b,a)\} \\
\psi_{3u} &= \frac{1}{\sqrt{2}}\{\phi_1(a,b) - \phi_1(b,a)\} \\
\psi_{4u} &= \frac{1}{\sqrt{2}}\{\phi_2(a,b) - \phi_2(b,a)\}
\end{aligned} \tag{4.16}$$

Since the perturbation V has u-symmetry the secular equation is given by

$$\begin{vmatrix}
-W^{(1)} & 0 & V_{13} & V_{14} \\
0 & -W^{(1)} & V_{23} & V_{24} \\
V_{31} & V_{32} & -W^{(1)} & 0 \\
V_{41} & V_{42} & 0 & -W^{(1)}
\end{vmatrix} = 0 \tag{4.17}$$

where $V_{ij} = \langle \psi_i , V \psi_j \rangle$. Solving Eq. (4.17) we obtain the lowest first-order energy $W_2^{(1)}$.

On the other hand the separated atoms N + N are in the same ^4S state at the limit as $R \to \infty$ and can be treated as a non-degenerate case since only one $^1\Sigma_g^+$ state exists. Hence in general we shall have

$$W_1(\infty) = W_1^{(0)}(\infty) + \lambda^2 W_1^{(2)}(\infty) + \cdots \tag{4.18a}$$

$$W_2(\infty) = W_2^{(0)}(\infty) + \lambda W_2^{(1)}(\infty) + \cdots \tag{4.18b}$$

Therefore the approximate crossing point at $R = \infty$ is

$$\lambda_c (R=\infty) \simeq - \frac{\Delta W^{(0)}(\infty)}{W_2^{(1)}(\infty)} \quad . \tag{4.19}$$

Since the denominator in Eq. (4.19) is the first order energy coefficient, $\lambda_c (R = \infty)$ may be smaller than $1/7$. (See Fig. 4b).

Hence we may conclude that the proposed perturbation theory can be applied when R is not too large.

4. Calculation of second-order energy and dipole moment

Using the method outlined in Section III.4,5, the second-order energy and the dipole moment have been calculated on a CDC 1604 computer. For the present calculation, it is convenient to replace the

spin-orbitals ϕ_i (i = 1,2, ..., 14) by the spatial orbitals ψ_i (i = 1,2, ..., 7) with $\phi_1 = \psi_1\alpha$, $\phi_2 = \psi_1\beta$, $\phi_3 = \psi_2\alpha$ and etc. In terms of the molecular orbitals ψ_i the second-order energy coefficient becomes [cf. Eq. (3.59)]

$$W^{(2)} = 2 \sum_{i=1}^{7} W_i^{(2)} \tag{4.20}$$

where

$$W_i^{(2)} = \sum_k a_{ik} \{ \langle \psi_i, v u_k \psi_i \rangle - \sum_{j \neq i}^{7} \langle \psi_j, v \psi_i \rangle \langle \psi_i, u_k \psi_j \rangle \} \tag{4.21}$$

and one-electron operator v is given by

$$v = Z_0 \left(r_B^{-1} - r_A^{-1} \right) . \tag{4.22}$$

The dipole moment expression [Eq. (3.65)] becomes

$$\langle \mu \rangle = \lambda \left[Z_0 R + 4 \sum_{i=1}^{7} \mu_i^{(1)} \right] + O(\lambda^3) \tag{4.23}$$

where

$$\mu_i^{(1)} = - \sum_k a_{ik} \{ \langle \psi_i, z u_k \psi_i \rangle - \sum_{j \neq i}^{7} \langle \psi_i, u_k \psi_j \rangle \langle \psi_j, z \psi_i \rangle . \tag{4.24}$$

Two sets of approximate Hartree-Fock molecular orbitals for N_2 were employed: (1) Nesbet's molecular wavefunctions[3] and (2) Ransil's best limited LCAO-MO[29]. For the functions $\tilde{f}_i$, four- and seven-term polynomials were employed:

$$\tilde{f}_{i\alpha} = -\frac{4Z_0}{R}\left(a_{i1}\eta + a_{i2}\xi\eta + a_{i3}\xi^2\eta + a_{i4}\eta^3\right) \qquad (4.25a)$$

and

$$\tilde{f}_{i\beta} = \tilde{f}_{i\alpha} - \frac{4Z_0}{R}\left(a_{i5}\xi\eta^3 + a_{i6}\xi^2\eta^3 + a_{i7}\eta^5\right) \qquad (4.25b)$$

where ξ and η are prolate spheroidal coordinates defined by

$$\xi = \frac{r_A + r_B}{R} \quad ; \quad \eta = \frac{r_A - r_B}{R} \quad . \qquad (4.26)$$

The variational coefficients a_{ij}, in Eqs. (4.25a) and (4.25b) were determined by the method described in Section III. 4.

It should be noticed that the operators $\mathcal{V}$ and $\mathcal{M}$ have u-symmetry, and therefore the functions $\tilde{f}_i$ should also have u-symmetry. Hence the off-diagonal terms in Eqs. (4.21) and (4.24) and also in Eqs. (3.51) and (3.58) vanish unless the spatial functions ψ_i and ψ_j have different inversion symmetry. Furthermore, the required molecular integrals $\langle \chi, \frac{\xi^m \eta^n}{\xi^2 - \eta^2} \chi' \rangle$ and $\langle \chi, \xi^m \eta^n \chi' \rangle$, where χ and χ' are Slater-type AO's centered at atom A or B, are easily expressed in terms of the auxiliary functions

$$A_m(t) = \int_1^{\infty} e^{-t\xi}\, \xi^m\, d\xi$$

$$B_n(t) = \int_{-1}^{+1} e^{-t\eta}\, \eta^n\, d\eta \quad . \tag{4.27}$$

The calculated results of the second-order energy, molecular energy and dipole moment are given in Table II. To compare the present results with those of a direct Hartree-Fock calculation, the molecular energy and dipole moment of Nesbet's[3] molecular wavefunction for CO are shown in Table III. To further show the dependence of the second-order energy and dipole moment on the choice of trial functions $\tilde{f}_i$, the coefficients in the four- and seven-term perturbation polynomials [Eqs. (4.25a) and (4.25b)], and also the orbital contributions to the second-order energy and dipole moment are given in Table IV.

The results for R = 2.068 B using Ransil's[27] and Nesbet's[3] molecular wavefunctions for N_2 as zeroth-order wavefunction show that the molecular properties in this calculation are not very sensitive to the choice of zeroth-order wavefunction. (See Table II). Furthermore, the convergence of the second-order energy was fairly good for the trial functions chosen, as can be seen in Tables II and IV.

The calculated molecular energy of CO is too low by 2.0 $\sim$ 6.0 H in the given range of R and decreases too fast as R becomes larger.

(See Tables II and III). Hence the calculated molecular energy does not give a minimum in the range of R investigated as implied by Eq. (2.12).

In an attempt to get an upper bound to the molecular energy E of CO , we approximate the ground state of CO as

$$\Psi = \Psi^{(0)} + \lambda \Psi^{(1)} \tag{4.28}$$

and the expectation value of the electronic Hamiltonian $H = H_0 + \lambda V$ is computed. The expectation value W(1) is given by

$$W(1) = W^{(0)} + \frac{\lambda^2 W^{(2)}}{1 + \lambda^2 S} \tag{4.29}$$

where $S = \langle \Psi^{(1)}, \Psi^{(1)} \rangle$ and the first- and third-order terms do not appear due to the u-symmetry of V. Now $\Psi^{(0)}$ is approximated by Nesbet's[3] molecular wavefunction for N_2 and $\Psi^{(1)}$ by that (with seven-term perturbation polynomial) determined by the uncoupled Hartree-Fock approximation. As shown in Table V, the estimated expectation value does not give an upper bound to the molecular energy E (cf. Tables I and II). This may be attributed to the defect of the uncoupled Hartree-Fock approximation for the present problem, since the zeroth-order wavefunction appears to be a good analytic approximation to the Hartree-Fock function.

The calculated dipole moment of CO is ridiculously large in magnitude compared with the results of Hartree-Fock calculations[3,4] and the experimental value.[5] The large magnitude of the dipole

moment is mainly due to the abnormally large contribution from the the $1\pi_u$ orbital. The polarity, $C^+ O^-$, agrees with the Hartree-Fock results at the equilibrium distance, but does not change sign in the vicinity of $R = R_e$, unlike the results of the Hartree-Fock calculation.

V. DISCUSSION

The present quantitative results of this theory for the isoelectronic molecules N_2 and CO are disappointing. The calculated molecular energy of CO is too low and does not give a minimum in the given range of internuclear separation R. It is shown, however, that the polarity of the electric dipole moment of CO agrees with the results of recent Hartree-Fock calculations[3,4] at the equilibrium separation, in spite of too large value in magnitude. It should be noticed that SCF-LCAO-MO approximation to the Hartree-Fock solution of N_2 was employed for zeroth-order wavefunction, and the uncoupled Hartree-Fock approximation was used to determine the second-order energy and the first-order wavefunction. The use of the coupled Hartree-Fock approximation might improve the result.

It is interesting to note that the molecular energy difference $\Delta E = E_{CO} - E_{N_2}$ may be obtained directly by means of the integral Hellman-Feynman theorem formulated by Kim and Parr.[28] In this case the theorem takes the form,

$$\Delta E = -\lambda^2 Z_0^2/R + \frac{\langle \Psi_{CO}, \lambda V \Psi_{N_2} \rangle}{\langle \Psi_{CO}, \Psi_{N_2} \rangle} \qquad (5.1)$$

where the first term is the nuclear-nuclear repulsion energy difference and Ψ_{CO} and Ψ_{N_2} may be approximated by Hartree-Fock wavefunctions for CO and N_2. The advantage of Eq. (5.1) is that it is valid whether or not λV is small. If the right hand side of Eq. (5.1) is expanded

in powers of λ , it reduces to the perturbation series, Eq. (2.9).

A related perturbation treatment for acetylene based on the isoelectronic molecule N_2 has been performed by Gilson and Arents.[29] However, in this case the first-order energy does not vanish, and it alone was calculated. The error involved was about twice that in the present paper, but in the opposite direction.

The significance of this theory is that it is a method of investigating molecular properties using perturbation theory and introducing the possibility of varying the nuclear charge. Furthermore, the perturbation operator [See Eq. (2.4)] has u-symmetry and is a sum of one-electron operators. The symmetry feature of the perturbation operator simplifies the actual calculation of the energy and other molecular properties for diatomic molecules as shown in Section IV. 4. The one-electron character of this operator allows the use of the well-developed theory of the one-electron perturbation effect. (Cf. Section III).

This theory might be extended to polyatomic molecules and crystals. For example, borazine, $B_3N_3H_6$, might be treated with benzene, C_6H_6 , as the unperturbed system, and borazon, $(BN)_\infty$, with diamond as the unperturbed system. For these cases, $\lambda = (Z_N - Z_B)/(Z_N - Z_B) = 1/6$. On the other hand, the diatomic molecule BF , with N_2 as the unperturbed system, would have $\lambda = 2/7$, which is probably too large for the theory to work.

ACKNOWLEDGEMENTS

The authors would like to thank Dr. T. H. Walnut for correcting an elementary but vital error in the original treatment. We are also very grateful to Dr. S. T. Epstein for numerous invaluable discussions about the Hartree-Fock approximations, and to Dr. J. O. Hirschfelder for helping to clarify the behavior of the energy curves in the presence of degeneracy.

APPENDIX

Energy difference between C + O atoms and N + N atoms (ground states) by $1/Z$-expansion

For an atom with charge Z and N electrons the electronic energy can be expanded by

$$\mathcal{E}(Z,N) = Z^2\epsilon^{(0)}(N) + Z\epsilon^{(1)}(N) + \epsilon^{(2)}(N) + \epsilon^{(3)}(N)/Z + \cdots \quad \text{(A1)}$$

For C atom (^3P) we must consider the degenerate configurations $1s^2 2s^2 2p^2$ and $1s^2 2p^4$. For the ^3P state of C atom with $M_L = 1$ and $M_S = 1$ the description[30] required are

(i) $1s\alpha, 1s\beta, 2s\alpha, 2s\beta, 2p_+\alpha, 2p_0\alpha,$

(ii) $1s\alpha, 1s\beta, 2p_+\alpha, 2p_+\beta, 2p_0\alpha, 2p_-\alpha$.

From each description, only one Slater determinant is needed. Hence we obatin a 2 x 2 matrix; and the secular equation is

$$\begin{vmatrix} H_{11} - \epsilon^{(1)}(6) & H_{12} \\ H_{12} & H_{22} - \epsilon^{(1)}(6) \end{vmatrix} = 0 \quad \text{(A2)}$$

H_{ii} is given by

$$H_{ii} = \sum_{a<b} (J_{ab} - K_{ab}) \quad \text{(A3)}$$

where J_{ab} and K_{ab} are the coulomb and exchange integrals between the hydrogenic spin-orbitals a and b. Crossley and Coulson[31] computed coulomb and exchange integrals for hydrogenic wave functions. The off-diagonal term is

$$H_{12} = \langle 2s\ 2s, \frac{1}{r_{12}}\ 2p_+ 2p_- \rangle \tag{A4}$$

where integration over the spin parts has been carried out. Then rearanging the integrand and using the Ufford and Shortley phase conversion[32]

$$H_{12} = \langle 2s\ 2p_+ , \frac{1}{r_{12}}\ 2s\ 2p_+ \rangle$$
$$= K(2s, 2p) \tag{A5}$$

since the wave functions are hydrogenic. Solving the secular equation (A2), we find $\epsilon^{(1)}(6) = 3.26\ H$. Hence for C atom

$$E(6,6) = 36\ \epsilon^{(0)}(6) + 6\epsilon^{(1)}(6) + \cdots$$
$$\simeq -34.45\ H\ . \tag{A6}$$

For the N atom (^4S) and O atom (^3P), there is no degeneracy. Hence we need only consider the configurations, $1s^2 2s^2 2p^3$ for N and $1s^2 2s^2 2p^4$ for O. Hence we obtain

$$N: \quad \mathcal{E}(7,7) = 49\,\epsilon^{(0)}(7) + 7\,\epsilon^{(1)}(7) + \cdots \simeq -49.15\,H \tag{A7}$$

$$O: \quad \mathcal{E}(8,8) = 64\,\epsilon^{(0)}(8) + 8\,\epsilon^{(1)}(8) + \cdots \simeq -66.70\,H. \tag{A8}$$

From Eqs. (A6), (A7) and (A8) we get

$$\begin{aligned}\Delta W &= \mathcal{E}(8,8) + \mathcal{E}(6,6) - 2\,\mathcal{E}(7,7) \\ &= \{64\,\epsilon^{(0)}(8) + 36\,\epsilon^{(0)}(6) - 98\,\epsilon^{(0)}(7)\} \\ &\quad + \{8\,\epsilon^{(1)}(8) + 6\,\epsilon^{(1)}(6) - 14\,\epsilon^{(1)}(7)\} + \cdots \\ &\simeq -2.85\,H.\end{aligned} \tag{A9}$$

This is to be compared with the empirical value calculated from the ionization potential[23] of each electron of N, C and O atoms,

$$\Delta W_{emp} = -3.74\,H. \tag{A10}$$

Hence

$$\Delta W_{cal.} - \Delta W_{emp.} = 0.89\,H = 24.2\ ev. \tag{A11}$$

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TABLE I

Experimental properties of Nitrogen and carbon monoxide

	R_e (A)	E_e (H)	D_e (ev)	k_e (10^6dyne cm^{-1})	μ_e(D)
N_2	1.094[a]	-109.586[b]	9.902[a]	2.296[a]	0.
CO	1.1281[a]	-113.377[b]	11.242[c]	1.906[a]	0.118(C^-O^+)[d]

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a. See reference 26.

b. See reference 2.

c. A. G. Gaydon, Dissociation Energies, revised edition (1953): D_e is corrected for zero-point energy.

d. See references 1 and 5.

TABLE II

Calculated energy and dipole moment of CO

R (B)		1.744393[c]	1.868[c]	2.068[c]	2.268[c]	2.391607[c]	2.068[d]
$E^{(0)}$ (H)		-108.86286	-108.94320	-108.97143	-108.92938	-108.88528	-108.63359
$\lambda^2 W^{(2)}$ (H)	a	-5.397	-5.833	-6.727	-7.889	-8.788	-6.724
	b	-5.401	-5.877	-6.776	-7.952	-8.869	-6.789
-1/R (H)		-0.573	-0.535	-0.484	-0.441	-0.418	-0.484
E (H)	a	-114.833	-115.311	-116.182	-117.259	-118.091	-115.842
	b	-114.837	-115.355	-116.231	-117.322	-118.172	-115.907
$\langle \mu \rangle$ (a.u.)[e]	a	-4.253	-5.966	-9.436	-14.363	-18.373	-12.607
	b	-4.251	-6.064	-9.562	-14.554	-18.644	-12.767

- - - - -

a. Four-term perturbation polynomial was used [Eq. (4.25a)].

b. Seven-term perturbation polynomial was used [Eq. (4.25b)].

c. Nesbet's[3] molecular wavefunction for N_2 was used.

d. Ransil's best limited LCAO-MO[27] was used.

e. Dipole moment was defined as negative for $C^+ O^-$. (See Section II.4).

TABLE III

Energy and dipole moment of Nesbet's[3] molecular wavefunction for CO

R (B)	1.808393	1.932	2.132	2.323	2.455607
E (H)	-112.66220	-112.72952	-112.75878	-112.73211	-112.70106
μ_x (a.u)	0.0830	-0.0032	-0.1562	-0.3246	-0.4342

TABLE IV

Expansion coefficients in the perturbation polynomials and orbital contributions to the second-order energy and dipole moment for R = 2.068. Zeroth-order wavefunction is Nesbet's[3] molecular wavefunction for N_2.

	Coefficients in $f_{i\alpha}$ [four-term perturbation polynomial, Eq. (4.25a)]						
Orbital	a_{i1}	a_{i2}	a_{i3}	a_{i4}	$w_i^{(0)}$ (H)	$\lambda^2 w_i^{(2)}$ (H)	$\lambda \mu_i^{(1)}$ (a.u.)
$1\sigma_g$	-1.2346	0.5160	0.0296	0.0367	-15.69623	-0.4875	-0.0020
$2\sigma_g$	-0.8774	0.1152	0.0406	0.1250	-1.48569	-0.3250	-0.1279
$3\sigma_g$	-1.0078	0.3561	-0.0131	-0.0291	-0.64278	-0.2378	-0.0511
$1\sigma_u$	-1.1463	0.5007	0.0369	0.0043	-15.69262	-0.4721	+0.0008
$2\sigma_u$	-1.0249	0.3575	-0.0042	-0.0445	-0.78581	-0.2257	+0.0771
$1\pi_u$	-1.7743	0.1897	-0.0250	0.4672	-0.62261	-0.8078	-1.3864

Coefficients in $f_{i\beta}$ [seven-term perturbation polynomial, Eq. (4.25b)]

Orbital	a_{i1}	a_{i2}	a_{i3}	a_{i4}	a_{i5}	a_{i6}	a_{i7}	$w_i^{(0)}$ (H)	$\lambda^2 w_i^{(2)}$ (H)	$\lambda \mu_i^{(1)}$ (a.u.)
$1\sigma_g$	-1.8557	0.8760	0.0015	0.4781	-0.1177	-0.0037	-0.1430	-15.69623	-0.4904	-0.0024
$2\sigma_g$	-0.8880	0.1832	-0.0009	0.0483	0.0142	-0.0048	0.0442	-1.48569	-0.3255	-0.1282
$3\sigma_g$	-1.1624	0.4380	0.0019	0.0906	-0.0062	-0.0074	-0.0411	-0.64278	-0.2429	-0.0615
$1\sigma_u$	-1.5426	0.8863	0.0014	0.1667	0.0156	-0.0035	-0.1489	-15.69262	-0.4748	+0.0005
$2\sigma_u$	-1.1523	0.4771	0.0019	-0.1315	0.1531	-0.0090	-0.0412	-0.78581	-0.2312	+0.0648
$1\pi_u$	-1.8991	0.1745	0.0006	0.8919	-0.2974	0.0032	-0.0395	-0.62261	-0.8116	-1.3903

TABLE V

Estimated expectation value of Hamiltonian with $\Psi = \Psi^{(0)} + \lambda \Psi^{(1)}$. $\Psi^{(0)}$ was approximated by Nesbet's[3] molecular wavefunction for N_2 and $\Psi^{(1)}$ by the function containing the seven-term perturbation polynomial determined by the uncoupled Hartree-Fock approximation.

R (B)	1.744393	1.868	2.068	2.268	2.391607
λ^2_S	0.0808	0.1066	0.1731	0.2819	0.3839
$\frac{\lambda^2_W(2)}{1+\lambda^2_S}$ (H)	-4.997	-5.311	-5.776	-6.203	-6.408
E (H)	-114.433	-114.789	-115.231	-115.573	-115.711

LIST OF FIGURES

1. Operators $\nu_i = r_{Bi}^{-1} - r_{Ai}^{-1}$ and $\mu_i = -Z_i$ (constant $\lambda Z_0 R$ is omitted.)
2. Schematic plot of the empirical electronic energy W(R) against the internuclear separation R for relevant states of CO and N_2.
3. Correlation of the electronic states.
   a. $R = \infty$
   b. $R \approx R_0$
   c. $R = 0$.
4. Schematic plot of the electronic energy W against the perturbation paramer λ. $W_1(1)$ and $W_2(1)$ are given by Eqs. (4.14a) and (4.14b), and $W_1(\infty)$ and $W_2(\infty)$ by Eqs. (4.18a) and (4.18b).
   a. $R \approx R_0$
   b. $R = \infty$.

Fig. 1

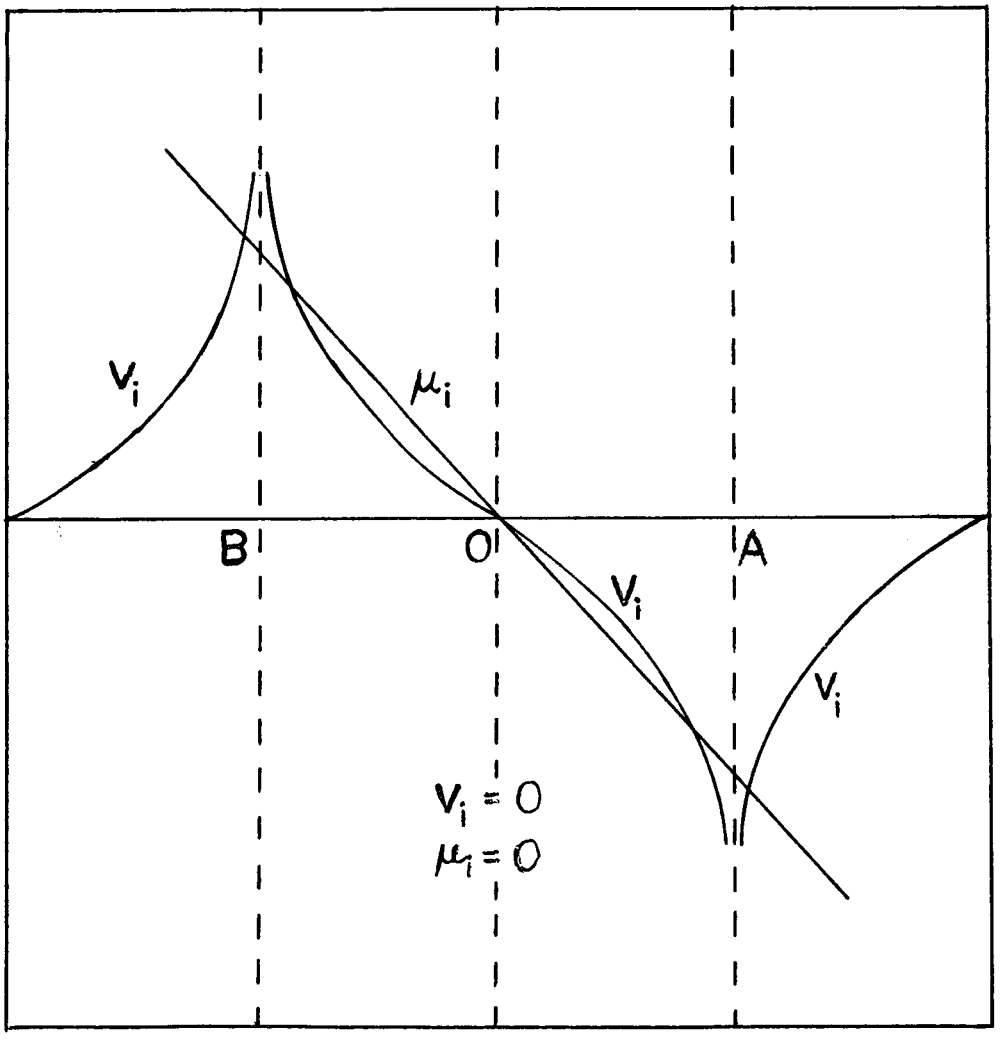


Fig. 2

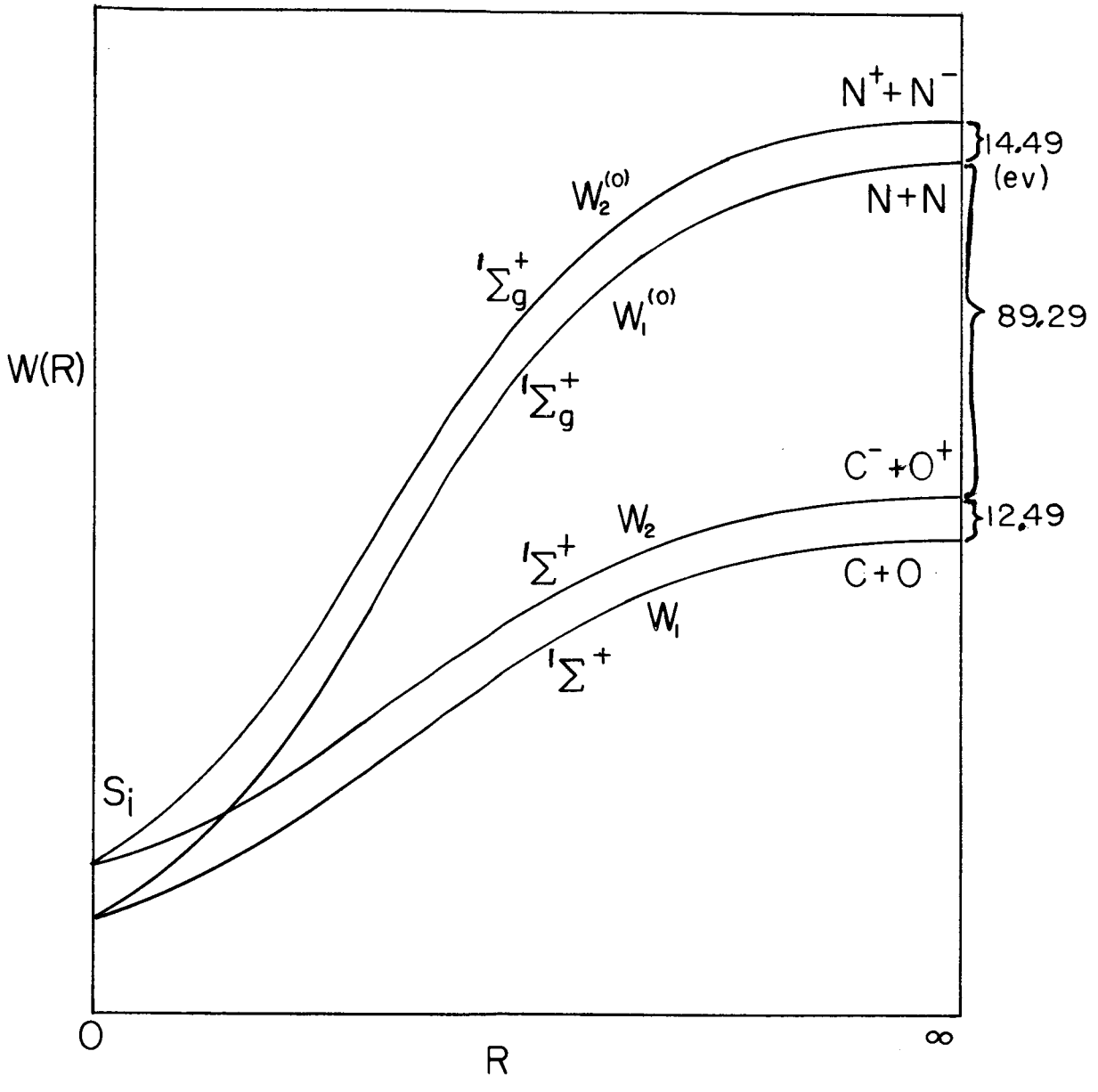

W(R)
O
R
∞
S_i
$^1\Sigma_g^+$
$W_2^{(0)}$
$W_1^{(0)}$
$^1\Sigma_g^+$
W_2
$^1\Sigma^+$
W_1
$^1\Sigma^+$
$N^+ + N^-$
N+N
$C^- + O^+$
C+O
14.49
(ev)
89.29
12.49

Fig. 3a

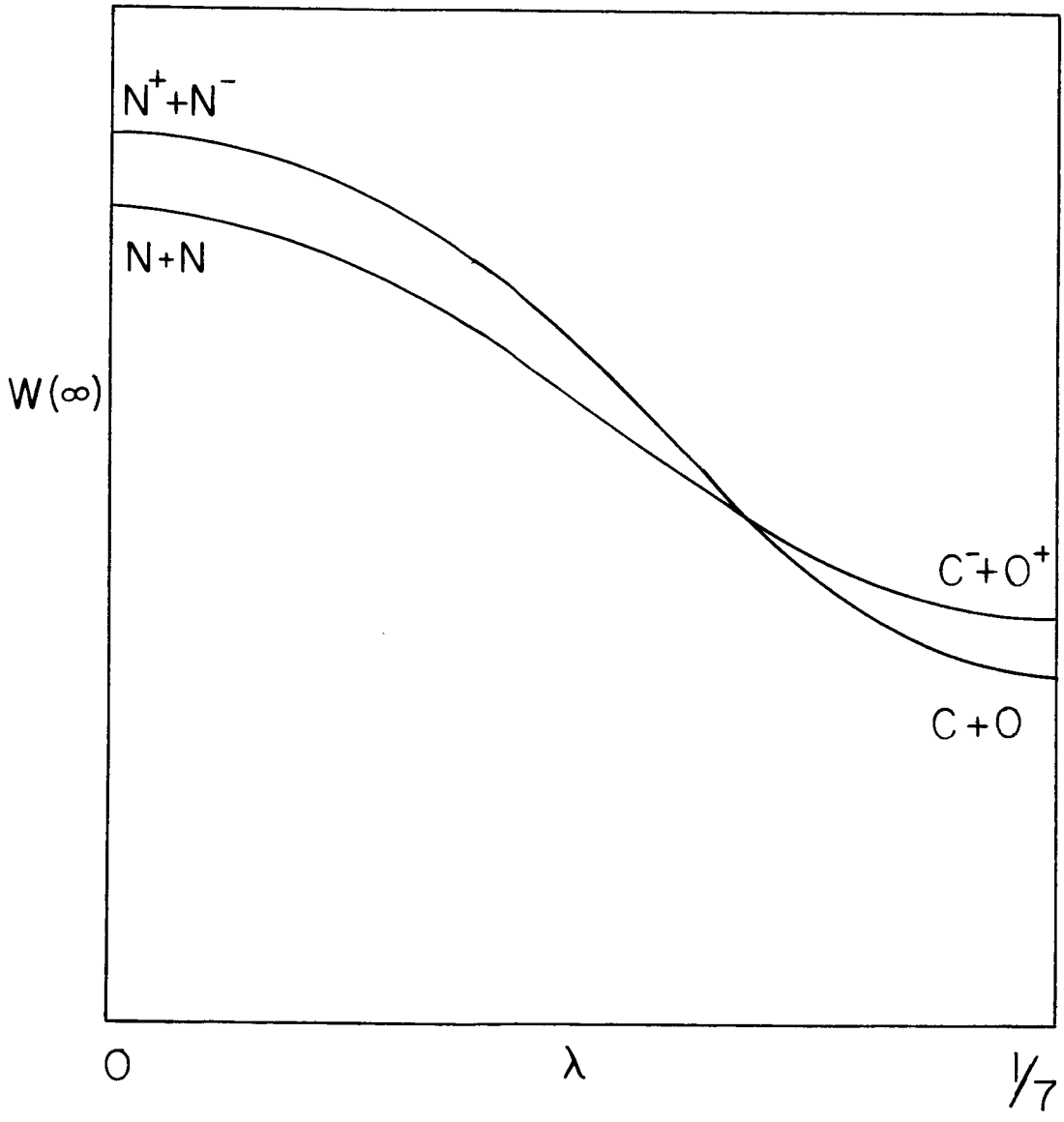


Fig. 3b

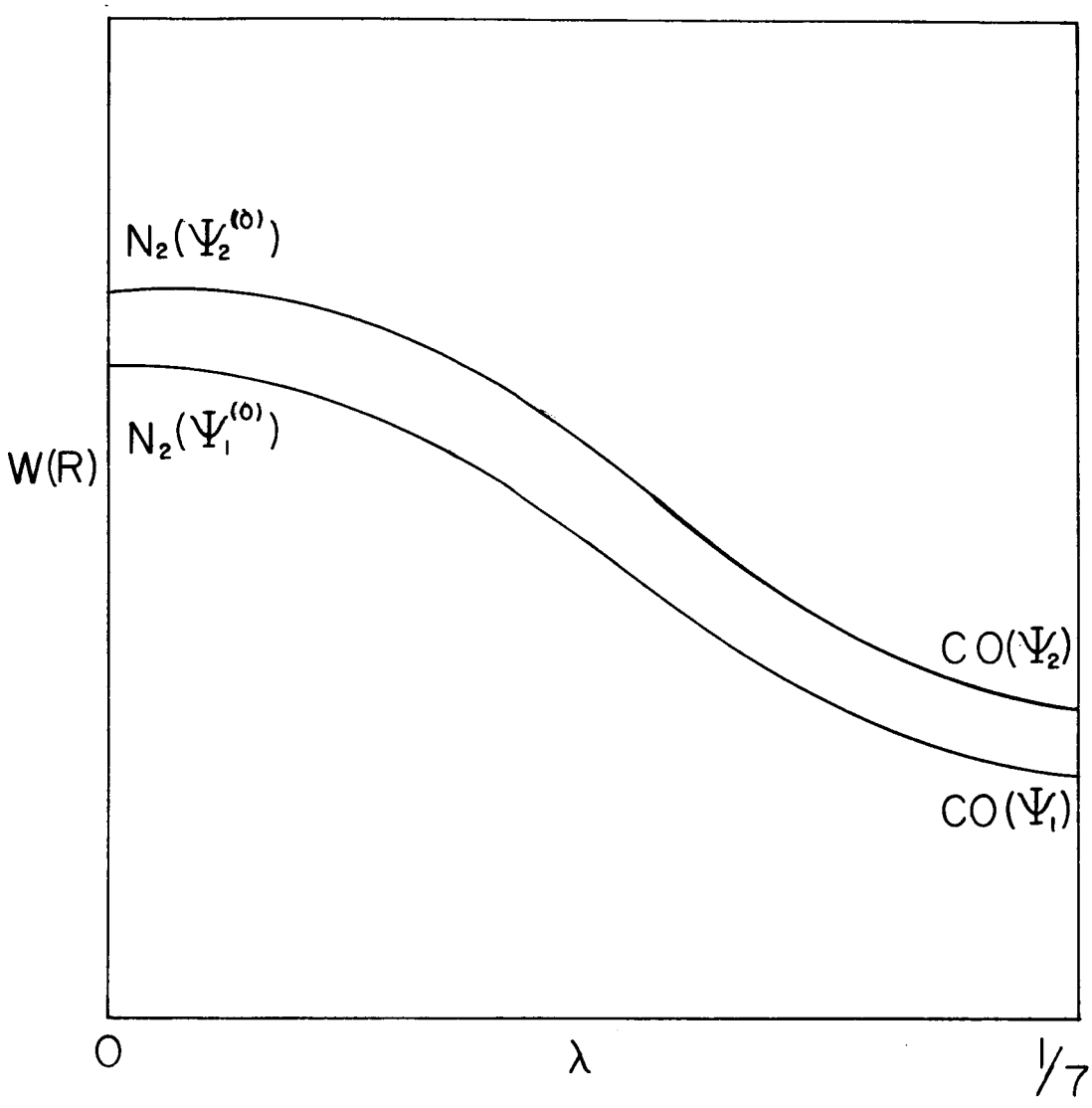
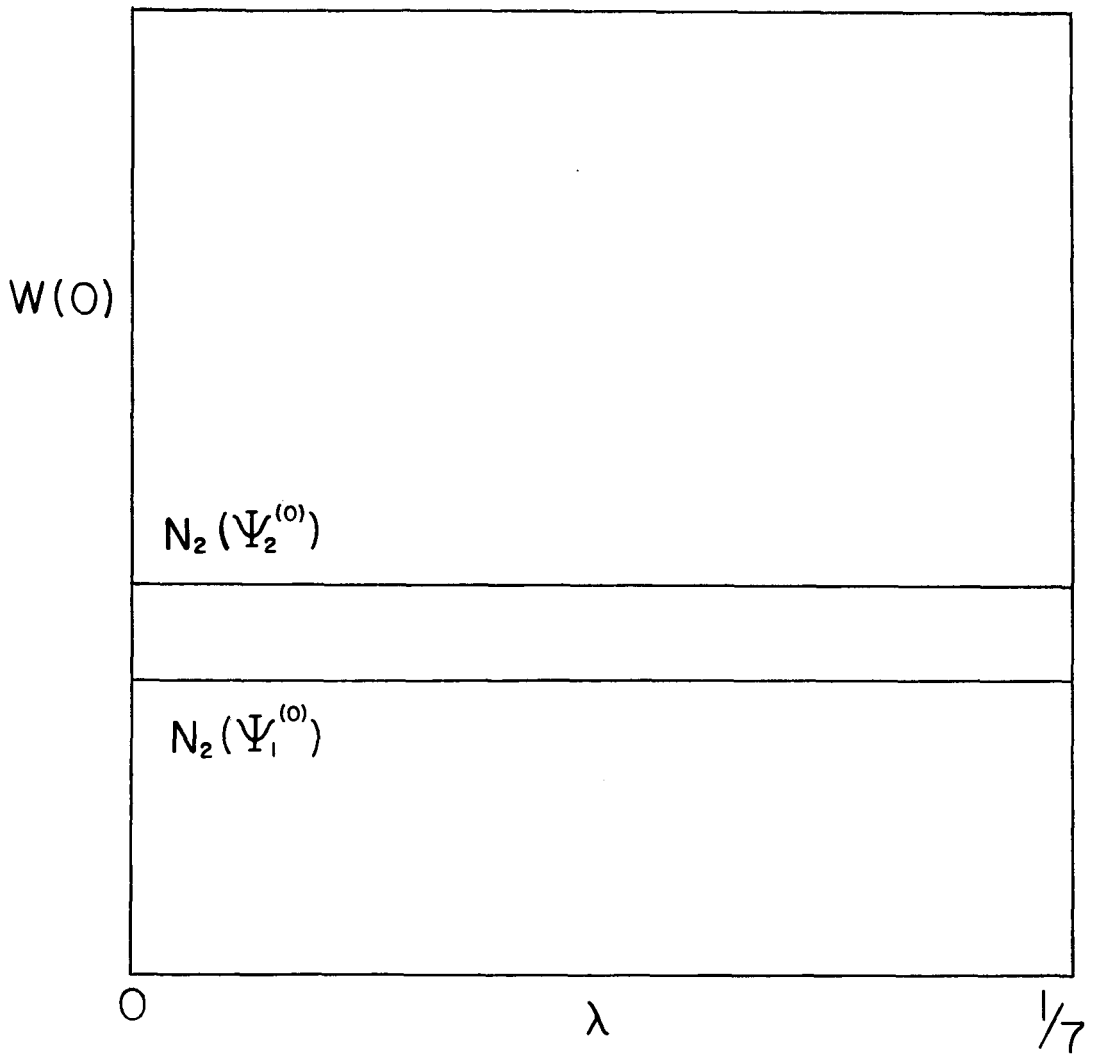


Fig. 3c



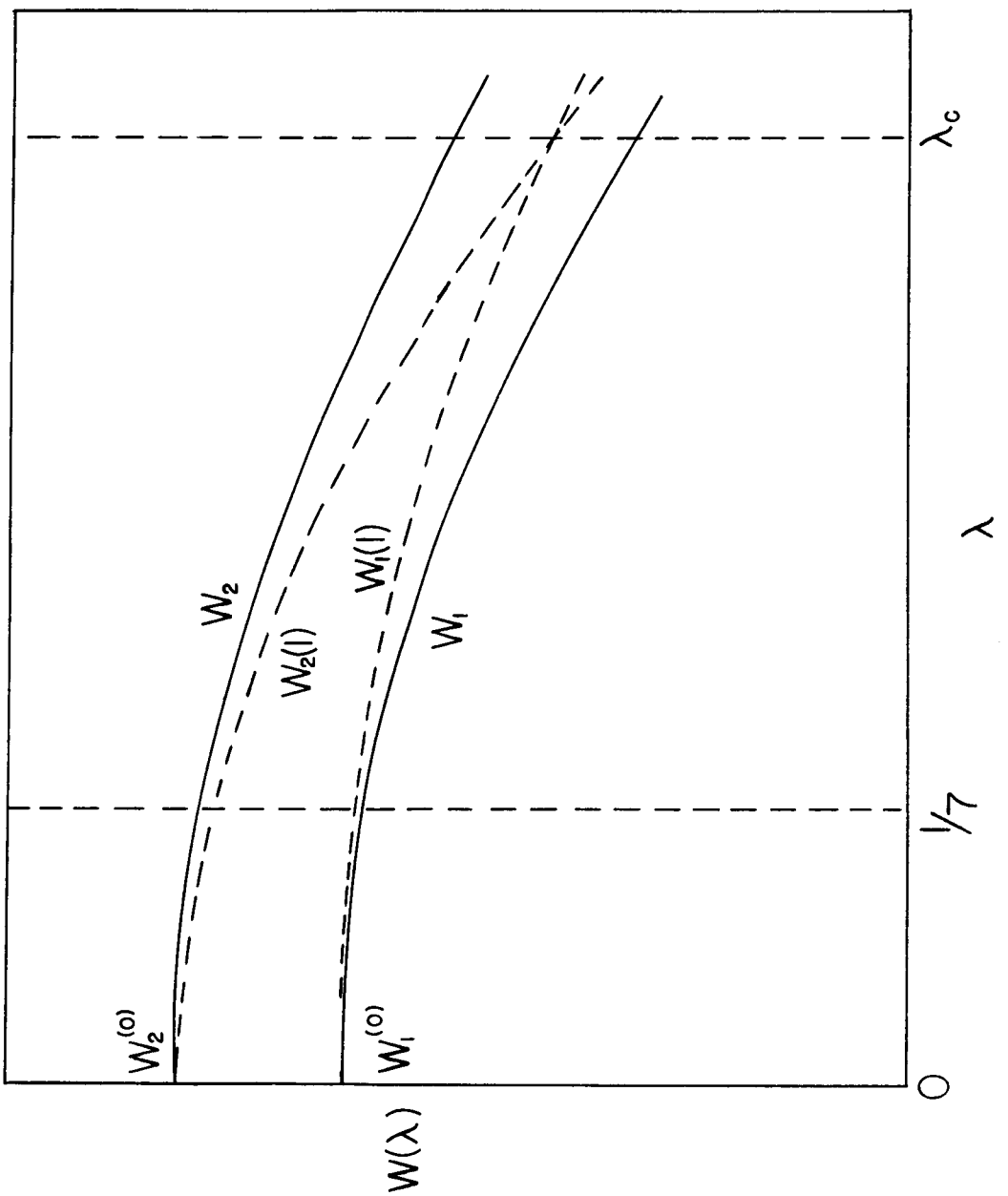


Fig. 4a

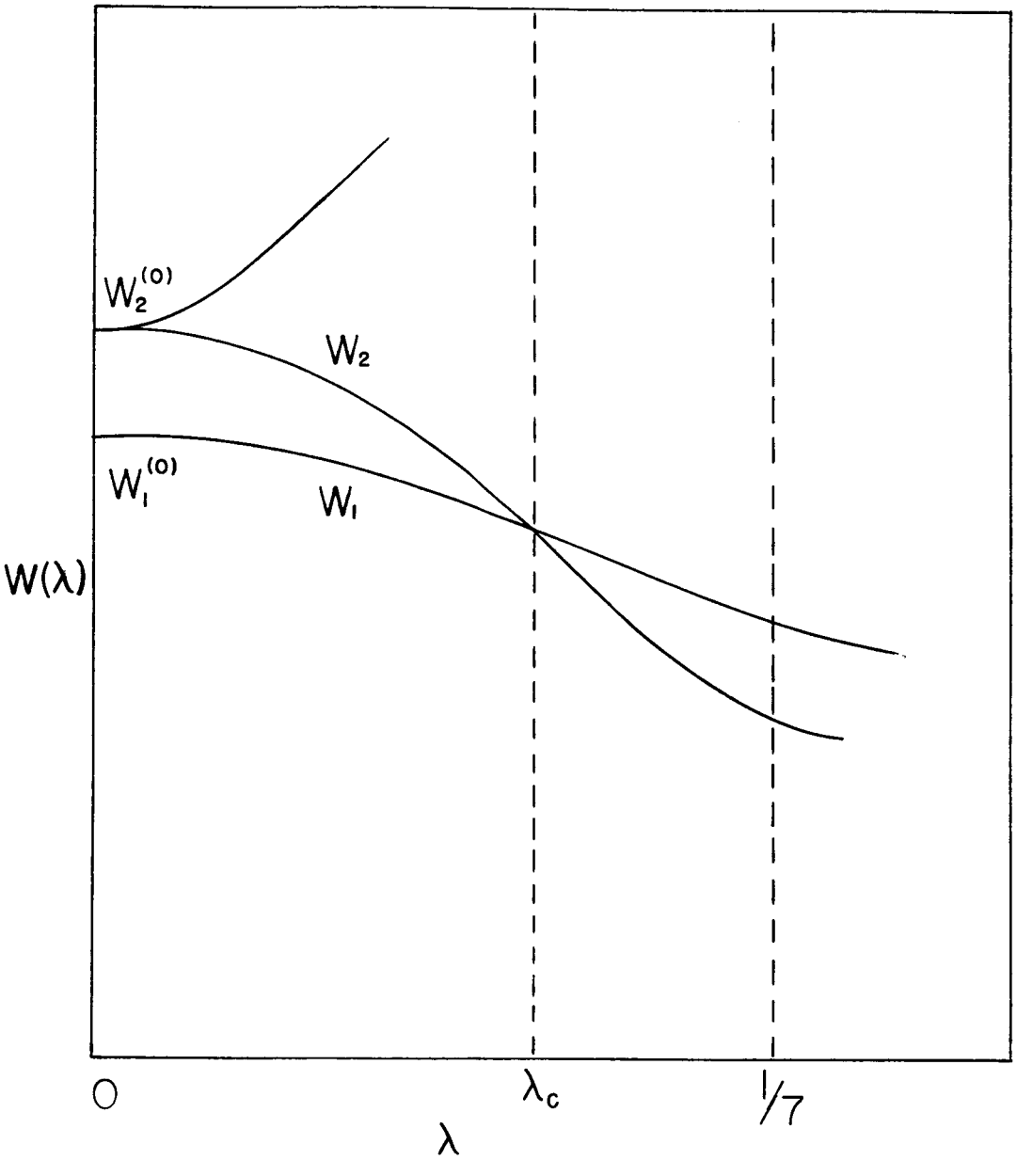



Fig. 4b